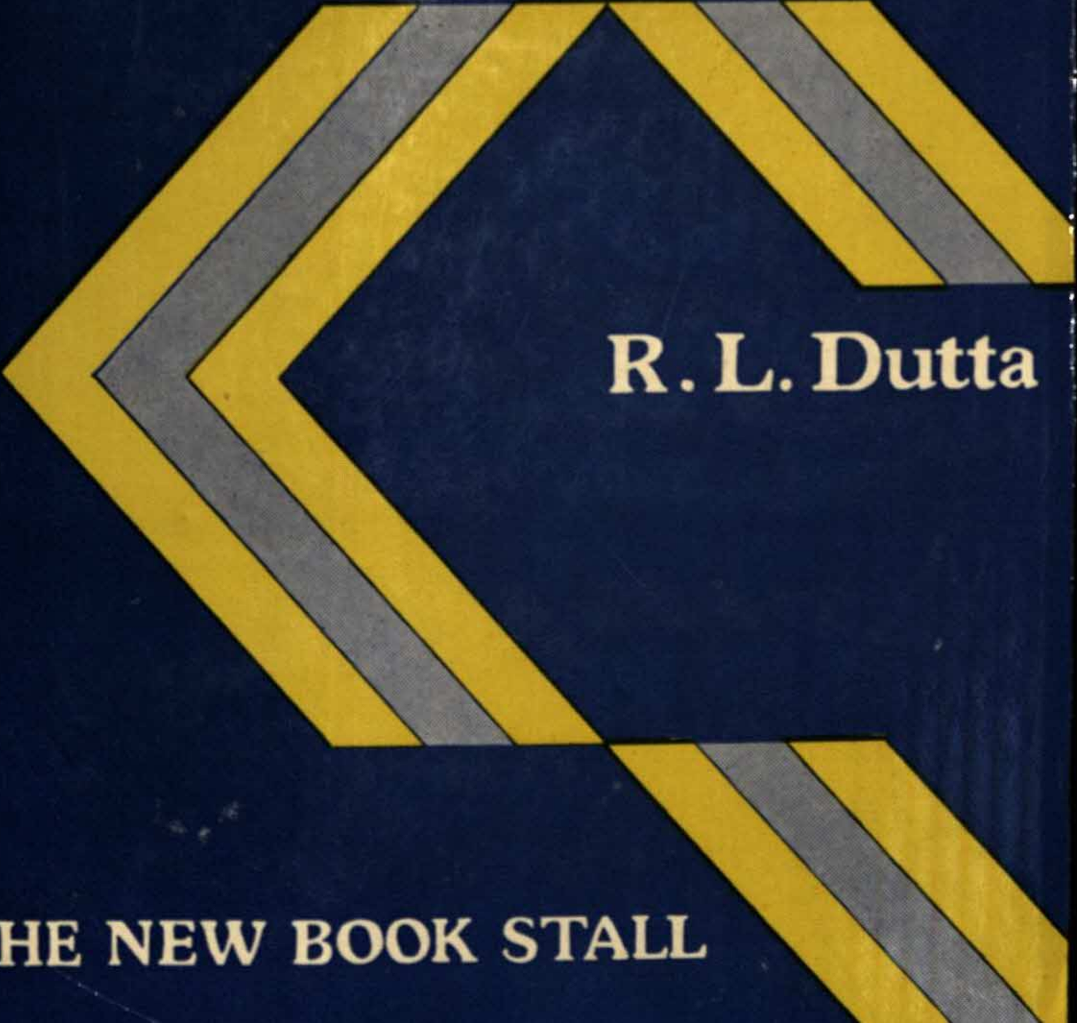
ELEMENTARY INORGANIC CHEMISTRY



R. L. Dutta

THE NEW BOOK STALL

ELEMENTARY
INORGANIC CHEMISTRY

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To
the dear departed mentor
Professor Priyadaranjan Rây
with faith and reverence

Experiments are the only means
of knowledge at our disposal.
The rest is poetry, imagination.

—*Max Planck*

PREFACE

The book is designed to serve undergraduate science students of India and Bangladesh. Since the book is addressed to B.Sc. (Pass) students I have not dished out materials which the young readers hardly need to master. The entire material may not be required by the students of a particular University. In including two Chapters on qualitative and quantitative analyses, I have endeavoured to present B.Sc. (Pass) Inorganic Chemistry in its entirety. This work is thus a two-in-one book.

I heartily thank my research associate Sri B. R. Das and my daughter Lopamudra for assistance. I acknowledge with pleasure my continuing association with The New Book Stall and Sadhana Press.

Any comments for further improvement from students and their respected teachers will be a sheer pleasure. Readers need not hesitate to point out where I could have done better.

R L DUTTA

Burdwan, West Bengal
July, 1983

CONTENTS

1 The Electronic Structure of Atoms 1
2 Radioactivity 26
3 The Periodic Table 45
4 Periodic Properties of Elements and Compounds 60
5 The Chemical Bond 68
6 Coordination Chemistry 86
7 Oxidation Reduction Reactions 99
8 Acids and Bases 119
9 Solute, Solvent and Solution 145
10 Allotropy, Polymorphism, Isomorphism and Isomerism 155
11 Atomic Weights and Molecular Weights 166
12 Determination of the Structures of Chemical Compounds 181
13 A Survey of Metal Extraction Procedures 191
14 Hydrogen 202
15 Group IA. The Alkali Metals 217
16 Group IIA. Magnesium and the Alkaline Earths 232
17 Group IIIB. Boron and Aluminium 245
18 Group IVB. Carbon, Silicon, Tin and Lead 258
19 Group VB. Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth 279
20 Group VIB. Mainly Oxygen and Sulphur 309
21 Group VIIB. The Halogens 339
22 The Noble Gases 359
23 Some Transition Elements 365
24 Group IB. Copper, Silver and Gold 400
25 Group IIB. *Z*inc, Cadmium and Mercury 414
26 Radium, Thorium and Uranium: Radioactive Elements 429
27 Determination of the Formula of Some Chemical Compounds 435
28 Qualitative Analysis 446
29 Quantitative Analysis 473
30 Some Chemical Problems 486
Appendix I Structures of Three Important Types of Ionic Compounds 497
Appendix II Types of Chemical Reactions 499
Appendix III Isomerism in Organic Compounds 510
Appendix IV Table of Atomic Weights 516
Addenda and Corrigenda 519
Index 521

ELEMENTARY
INORGANIC CHEMISTRY

CHAPTER 1

THE ELECTRONIC STRUCTURE OF ATOMS

The young readers might as well set tune to the proceedings by asking the question : what really is inorganic chemistry ? The answer to this simple question is not that simple — particularly when the subject has grown so vastly. A contemporary definition of the subject runs as : Inorganic Chemistry is the science of the chemical behaviour and of the chemical principles underlying the physical behaviour of all wholly or partially inorganic substances. This definition is indeed vast in its scope. In this book ELEMENTARY INORGANIC CHEMISTRY an endeavour will be made to familiarise the young readers with the basic principles that are essential for an appreciation of the properties of the chemical elements and their compounds. This will then be followed by a concise description of the chemistry of the selected elements.

The most basic of the principles is undoubtedly the electronic structure of atoms. Just as Rome was not built in a day, it took chemists and physicists many many years to arrive at the solid foundation relating to the electronic structure of atoms. The presentday knowledge will be developed chronologically as far as practicable.

1.1. DALTON PROPOSES HIS ATOMIC THEORY

There were people who believed in the particle nature of matter. Among these may be mentioned the Greek philosopher Democritus (400 B.C.) and the great Isaac Newton (1642-1727). But to Dalton, an outstanding school teacher, must go the credit of formulating the basic ideas of the atomic theory :

1. All elements are made up of small particles. These small particles are called *atoms*. All atoms of one and the same element have the same properties. In other words an element is made up of atoms of the same kind.

2. Atoms of one and the same element have the same mass. Atoms of different elements have different masses.

3. Atoms of different elements differ in their chemical nature. New chemical compounds are formed as a result of reactions between atoms of different elements. During the formation of new chemical compounds atoms of the combining elements react in definite proportion.

4. Atoms are indivisible. No chemical reactions can bring about the breakdown of atoms. Nor is it possible to transform an atom of a particular element into an atom of another element.

1.2. A SUMMARY OF THE CURRENT THINKING

At the turn of this century new things started happening. Evidence on the electrical nature of matter came from studies on gas discharge phenomena. Prior to this

Faraday's classic experiments on electrolysis provided the first clue to the electrical nature of atoms. Then came the classic experiments of Thomson leading to the identification of electron, the unit of negative electricity, and that of Rutherford demonstrating that atoms are composed of a central core of positively charged nucleus surrounded by electrons. Finally there appeared on the scientific horizon a host of brilliant theoreticians Bohr, Pauli, Heisenberg, Planck, Schrodinger and others who contributed to our knowledge of the arrangement of electrons around the nucleus.

Currently we know that atoms are composed of a nuclear core comprising two fundamental particles called proton and neutron. Outside this positive core are the electrons. Earlier the electrons were supposed to be moving in a fixed path, called the orbit, about the nucleus. Now this concept has been abandoned in view of the fact that the electron is so tiny a particle that it is not possible by any technique to locate the position i.e. its path with certainty. There will always remain an element of uncertainty with respect to its position and momentum. As a result the concept of probability contours, for electron motion about the nucleus has been accepted. The most probable space of finding the electron is termed an *orbital.*

Chemical reactions result from transfer of electrons from one atom to another or from sharing of electrons by two or more atoms. Thus electrons are the real vehicles through which chemical interactions occur.

1.3. DISCOVERY OF THE ELECTRON AND ITS PROPERTIES

1.3.1. Probes into the passage of electricity through gases. As long back as 1750 Watson, in England, observed that a flow of charge occurred through a sealed tube provided the gas pressure inside was low enough. Gases are normally non-conductors of electricity but they do conduct electricity when subjected to high voltages at quite low pressure (around 0.001 atm.). Tubes in which such experiments are conducted are known as gas discharge tubes. Gas discharge tubes are provided with metallic electrodes : one is connected to the positive terminal of an outside source of potential difference—this is called the *anode*. The other electrode is connected to the negative terminal and is termed the *cathode*. A modern neon sign tube is a fine example of a gas discharge tube. The electrodes are placed at either ends of the sign tube and the tube contains neon gas at low pressure. On the application of a potential difference of several thousand volts between the electrodes electricity flows through the gas and a red glow appears inside the tube.

By 1890 various types of experiments had been carried out with discharge tubes of different size and shape. By then it was firmly established that the glow in such tubes are due to rays originating from the cathode and which travel in straight lines and strike either the anode or the glass surface of the tube depending on the shape of the tube and the positions of the electrodes.

In 1897 Thomson added new dimension to the gas discharge tube. He decided to examine the nature of these cathode rays in an applied electric and magnetic field. He placed two parallel metal plates in the path of these cathode rays such that he could set a potential difference between the plates. He amazingly observed that the cathode rays were shifted from their original course and appeared to get attracted by the positively charged plate. This shift led him to conclude that the cathode rays were negatively charged. He also subjected these rays to a magnetic field in the absence of the applied electric field. This time he observed the shift to be in a direction opposite to that with the electric field on. This behaviour was comparable to the observation that a wire carrying a current is acted upon by a magnet so as to push the wire away from the magnet.

From a long series of experiments Thomson arrived at the following conclusions :

1. Since the cathode rays get bent towards the positive plate they must be negatively charged.

2. Behaviour of the cathode rays remained the same irrespective of the nature of the gas inside the discharge tube.

3. When some object was placed on the path of the rays a shadow of the object was cast on the opposite wall.

4. Cathode rays warm up an object they strike.

5. When the potential difference to produce the cathode rays was increased the deflection of the rays from the poles of the magnet was also increased.

6. When the potential difference to produce the cathode rays was increased the deflection of the rays towards the positively charged plate of the applied electric field was decreased.

Thomson could realise that the last two observations must be connected with the mass and the velocity of the cathode rays. The cathode rays must be travelling with greater velocity on increasing the potential difference. Consequently the force produced by the deflecting electric field finds lesser time to influence the cathode rays.

Thomson now realised that the classic experiments of Faraday on electrolysis carried out as long ago as 1833 could help him in a big way. The ratio of charge to mass of various ions had been obtained from the electrolysis experiments. Thomson now recognised that a determination of charge to mass (e/m) ratio for the cathode rays would enable him to establish the identity of these rays. The cathode rays were named *electrons.*

1.3.2. Thomson determines the (e/m). Thomson made use of the apparatus (Fig 1.1) for the measurment of the (e/m) of the cathode rays i.e. the electrons. The discharge tube had a cathode and a perforated anode such that the cathode rays could emanate from the surface of the cathode and travel straight out of the anode. Thereafter his

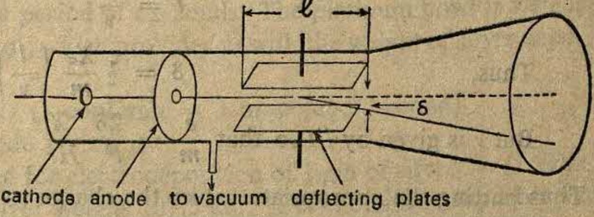

Fig 1.1. Schematic representation of Thomson's apparatus for measurement of (e/m) of the cathode rays. The magnetic field is not shown.

imaginative design had two parallel electric plates between which he could apply considerable high voltage. He had also two magnet pole pieces so arranged outside the discharge tube that the magentic field was at right angles to the applied deflecting electric field. The fields could be applied together or independent of one another. In the absence of any of the applied fields the cathode rays travelled straight and created a luminous spot on a light sensitve ZnS screen. Either of the two fields applied alone deflected the cathode ray beam from its original horizontal path i.e. the position of the original spot on the ZnS screen got displaced. But the effect produced by the magnetic field was in opposition to that produced by the electric field. Thus if the electric field were first applied and held constant, then the the magnetic field could be so adjusted that the displaced spot on the ZnS screen could be brought back to its original position. When the electric field, X, and magnetic field, H, were adjusted to achieve that *no displacement condition*, then the force on the particles of cathode rays due to the electric field, Xe, was equal to that due to the magnetic field, Hev. Thus the velocity of the particles while moving through the electric field could be determined :

$$Hev = Xe \; ; \quad v = \frac{X}{H}$$

In the next step of his experiment Thomson had the magnetic field removed and studied the displacement of the spot on the application of the electric field alone. As the particles pass through the deflecting electric field they experience a deflection, δ, from the horizontal trajectory. The electric force is given by the product of mass and acceleration :

$$Xe = \text{force} = \text{mass} \times \text{acceleration} = ma$$

$$a = \frac{Xe}{m}$$

The deflection, δ, can be equated to the acceleration and the time, t, the particles spend between the deflecting plates :

$$\delta = \tfrac{1}{2}\, a\, t^2$$

the value of t can be evaluated from a knowledge of the length, l, of the deflecting plates and velocity, v, of the particles :

$$t = \frac{l}{v}$$

Thus, $$\delta = \frac{1}{2}\,\frac{Xe}{m}\left(\frac{l}{v}\right)^2$$

But v is given by l/t so that $\dfrac{e}{m} = \dfrac{2\delta}{l^2}\,\dfrac{X}{H^2}$

Thus putting the appropriate values the charge to mass ratio of the cathode ray particles was evaluated. The currently accepted value of the (e/m) of the cathode rays i.e. the electron is :

$e/m = 5.274 \times 10^{17}$ esu/gm $= 1.76 \times 10^{8}$ coulomb/gm ; (1 coulomb $= 3 \times 10^{9}$ esu).

1.3.3. Determination of the charge of the electron from electrolysis. As a result of extensive series of studies on electrolysis of many salts Faraday was able to propose the two famous laws of electrolysis :

First Law : The weight of a given amount of material deposited, evolved or dissolved at an electrode is directly proportional to the quantity of the electricity passed through the electrolyte.

Second Law : The weights of the different materials deposited, evolved or dissolved at an electrode as a result of electrolysis of different chemical substances by a fixed amount of electricity are directly proportional to the equivalent weights of these chemical substances.

An in-depth look at the second law tells us that since a fixed amount of electricity brings about the electrolysis of equivalent amounts of different chemical substances, then equivalent amounts of different chemical substances must contain equal number of electrical charges. Thus the second law of electrolysis is in a way parallel to the laws of chemical combination, which had helped Dalton to propose his atomic theory. It follows that a fixed number of atoms or ions must respond to a fixed quantity of electricity. Thus in the process of electrolysis one atom or ion must lose or gain an integral number of electrical particles. From Thomson's experiments we have already seen that the tiny particles of negative electricity are the electrons.

Our concern in this section is to see how we can evaluate independently the charge associated with an electron. We know that salts of those elements placed below hydrogen in the electrochemical series can be electrolysed easily. Thus on electrolysis of an aqueous solution of silver nitrate silver is deposited at the cathode. As we know valency of silver in silver nitrate is $+1$. On electrolysis the monopositive silver ion must be moving to the cathode where it will take up an electron—the smallest unit of negative electricity—and would get deposited as silver metal : $Ag^+ + e \rightarrow Ag$. From mole concept we know that a mole stands for a fixed number of atoms, molecules or ions. This mole represents the Avogadro number i.e. 6.023×10^{23}. If we now determine the quantity of electricity that would lead to the deposition of a gm. mole/gm. atom of silver at the cathode—that would also give us the total quantity of electricity associated with a mole of electrons. This quantity of electricity has a special name, *faraday*.

Let us assume that a current of strength I ampere is passed through an aqueous soultion of silver nitrate for a period of t seconds. The platinum bowl is weighed before and after the experiment, which provides us with the weight of silver deposited at the cathode.

Number of coulombs $= I \times t$ (1 coulomb $=$ 1 ampere $\times$ 1 second)

Silver deposited at the cathode $=$ x gm

Number of coulombs required for electrodeposition of 1 gm of silver $= (I \times t)/\text{x}$

We know that 1 gm atom silver weighs 107.9 gm. It is experimentally observed that electrodeposition of 1 gm of silver requires 894.5 coulombs. So for electrodeposition of 1 gm atom/1 gm mol of silver we need :

$$\frac{894.5 \text{ coulombs}}{1 \text{ gm}} \times \frac{107.9 \text{ gm}}{1 \text{ mole}} = \frac{96{,}500 \text{ coulombs}}{1 \text{ mole}}$$

Since silver ion is monopositive electrodeposition of 1 gm mole of silver will need one mole of electrons. Hence 96,500 coulombs of electricity must stand for the charge of 1 mole of electrons. Therefore charge associated with a single electron is given by :

$$\begin{aligned}\text{charge of an electron} &= 96{,}500 \text{ coulombs}/(6.023 \times 10^{23}) \\ &= 1.60 \times 10^{-19} \text{ coulomb/electron} \\ &= 4.80 \times 10^{-10} \text{ esu/electron}\end{aligned}$$

We will conclude this section by mentioning that no other particle carrying smaller negative charge than the electron has ever been discovered. Therefore the absolute charge of 4.80×10^{-10} esu has been taken as the unit of electricity. Thus $-1e$ would mean an electron which has associated with it an absolute charge of 4.80×10^{-10} esu. On the contrary $+1e$ would stand for a particle which has the same absolute charge as that of the electron but the charge is positive in nature.

1.3.4. Determination of the mass of an electron. Now that we have two independent experiments giving us the *e/m* as also the *e* of an electron the calculation of its mass is a simple affair.

$e/m = 1.76 \times 10^{8}$ coulombs/gm ; $e = 1.60 \times 10^{19}$ coulomb

$$\begin{aligned}\text{Therefore mass, } m\text{, of the electron} &= \frac{1.60 \times 10^{-19} \text{ coulomb}}{1.76 \times 10^{8} \text{ coulomb/gm}} \\ &= 9.108 \times 10^{-28} \text{ gm}\end{aligned}$$

The mass of the electron as given above is known as the *rest mass*. The velocity of electrons is usually around 3.0×10^{9} cm/sec. Compared to the velocity of light the electrons may be taken to be virtually at rest. It may be mentioned at this point that finer experiments carried out on the determination of (e/m) of electrons of varying velocity (such as the beta particles emitted by different radioactive elements) had shown that (e/m) decreased with increasing velocity. Since the charge e may reasonably be assumed to be constant the inevitable conclusion is that the mass m of the electron increases with increasing velocity.

1.4. A PROBE INTO THE EXISTENCE OF THE PROTON AND ITS PROPERTIES

We have so far been able to convince ourselves about the existence of the unit of negative electricity, namely the electron. Since matter as a whole is neutral it follows that the smallest building block of all elements, namely the atom, must also be neutral. A search for a positively charged particle reasonably began. Thomson was able to provide us with the necessary data on the electron by operating his gas discharge tube apparatus at quite low pressure. Before the advent of Thomson, Goldstein carried out some discharge tube experiments with a perforated cathode instead of perforated anode. He was surprised to see that a beam of rays emanated from the anode and travelled towards the cathode. In these experiments the gas pressure inside the discharge tube was higher than in the case of the cathode ray discharge tubes. Thomson later demonstrated that the lightest of these particles had (e/m) around 28×10^{13} esu/gm. It was also established that these particles were positively charged and that the magnitude of their charge was the same as that of the electron. These particles were termed *protons*.

The protons were shown to have a close connection with the hydrogen atom. The weight of one gram-atom of hydrogen is 1.008 gm. Therefore the weight of one atom of hydrogen is $1.008/(6.023 \times 10^{23})$ gm $= 1.6736 \times 10^{-24}$ gm. As against this an electron weighs only 9.1×10^{-28} gm. Thus compared to an electron an atom of hydrogen is $(1.6736 \times 10^{-24})/(9.1 \times 10^{-28}) \simeq 1836$ times heavy. Later studies have revealed that the proton results when a hydrogen atom is stripped of its electron. A proton plus an electron gives the hydrogen atom.

1.5. THE NUCLEUS OF THE ATOM

1.5.1. Thomson proposes his model of the atom. By 1898 some ideas about the constituents of the atom have accumulated. The concern was that how the entire atom looked like. The size of the atom could be guessed from an idea of the atomic volume. Gram-atomic volume is expressed in cm^3/gm-atom. This, when divided by the mole of atoms i.e. the Avogadro number 6.023×10^{23} provides the volume of an atom as of the order of roughly 10^{-24} cm^3. Assuming that the atom is spherical the volume of a sphere is given by $(4/3)\ \pi\ r^3$ and hence the size of the atom i.e. the radius works out to be of the order of 10^{-8} cm. For electroneutrality the atom must have both electrons and protons. Again the protons were shown to be about 1836 times heavier than the electrons. Since electrons were so very light Thomson proposed that almost the entire mass of the atom was due to the positive particles. Further since the entire mass came from the positive particles, it appeared to Thomson that the positive particles were responsible for the volume of the atom. To sum up, Thomson assumed that an atom was a sphere of positive electricity of about 10^{-8} cm radius, in which were embedded the electrons in a way as to give a stable electrostatic arrangement.

1.5.2. Rutherford performs his scattering experiments. In 1911 Rutherford performed a series of most brilliantly conceived experiments at the McGill University. He bombarded thin gold foil (approximately 10,000 atoms thick) with fast moving alpha particles produced by the radioactive decay of radium. Ruther-

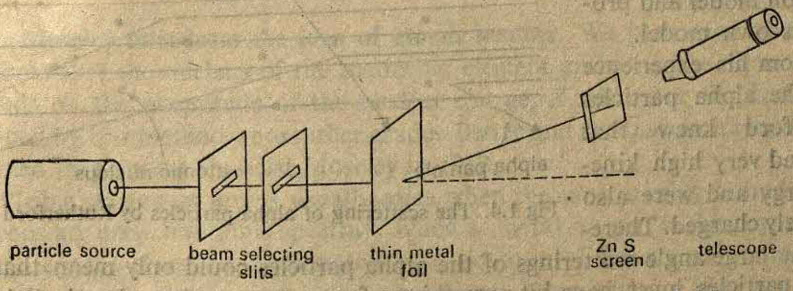

Fig 1.2. Rutherford's apparatus for observing the scattering of alpha particles by thin metal foil

ford had already established that the alpha particles were doubly charged helium ions (i.e. helium atom minus two electrons). The trajectory of the alpha particles was followed by the flash they produced when they collided with light-sensitive ZnS screen. The ZnS screen was so mounted that it could be moved around the target gold foil in a circle so that the path of scattered alpha particles could be examined from all directions. The apparatus was enclosed in a vacuum chamber so that flashes could not result from the impact of the alpha particles upon gaseous molecules. A telescope was mounted behind the screen to detect the small flashes produced when the alpha particles hit the ZnS screen (Fig. 1.2).

The results obtained with this apparatus demonstrated that most of the alpha particles passed through the gold leaf almost undeviated. But a very few scintillations occurred at many different angles. Some of these angles were as large as 180° i.e. these alpha particles were really sent back along its original track by the gold foil.

1.5.3. Rutherford proposes his model of the atom and rejects that proposed by Thomson. We recall that the Thomson model assumes that the atom is a sphere of positive electricity with the electrons embedded in this sphere. Furthermore the atom is assumed to be of uniform density. If this be the case then the alpha particles must meet a very much larger sphere of positive electricity. The sphere being assumed larger the density of positive electricity over the sphere must be quite small. We shall therefore expect that the alpha particles will be deviated at most by only small angles. Thomson model does not provide any explanation of the large angle scatterings. Therefore Rutherford had to reject the Thomson model and propose his own model.

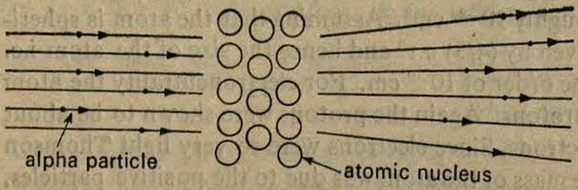

Fig 1.3. The scattering of alpha particles by Thomson atoms

From his experience with the alpha particles Rutherford knew that these had very high kinetic energy and were also positively charged. Therefore the large angle scatterings of the alpha particles could only mean that the alpha particles must have hit something of enormous positve electrical charge. He also realised that the enormous repulsive force must have been exerted by

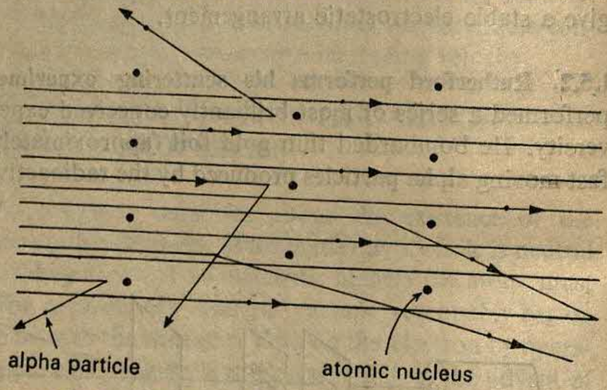

Fig 1.4. The scattering of alpha particles by Rutherford atoms

a body of large mass. It could be understood easily that the tiny electrons would be swept aside by the heavy alpha particles. Furthemore, since only a few alpha particles were deflected back by large angles it could only mean that the large positive electrical charge was confined to very small space inside the atom.

Thus in contrast to the Thomson model of the atom being a sphere of uniform mass and charge density, the Rutherford atom was highly non-uniform. (1) The positive charge was concentrated in a very small space, called the *nucleus*, The nucleus was tiny in dimension but very heavy indeed, since the entire mass was concentrated in this nucleus. (2) As most of the alpha particles went through either undeviated or were scattered through small angles, it meant that most of the inside of the atom was empty. (3) In this empty space were included the electrons. Rutheford further proposed that the electrons were not stationary. If the electrons were stationary then these would be gradually dragged on to the nucleus, thus destroying the atomic structure itself. He therefore suggested that the electrons were moving around the nucleus such that the centrifugal force was balanced by the attractive force between the nucleus and the electrons.

The dimension of the nucleus could also be calculated from the alpha ray scattering experiment. An alpha ray particle is deflected by 180° only when it makes a head-on collision with the positively charged nucleus. Under this situation the initial kinetic energy of the alpha particle must have been equal to the Coulombic potential energy of repulsion between the alpha particle and the positive nucleus.

$$\tfrac{1}{2}mv^2 = \frac{zZe^2}{r_{min}}$$

(v, m and ze are the velocity, mass and the charge respectively of the alpha particle while Ze represents the charge associated with the nucleus. r_{min} stands for the distance of closest approach of the nucleus and the alpha particle).
For alpha particles obtained from radium, $v = 1.6\times10^9$ cm/sec, $e = 4.8\times10^{-10}$ esu, $m = 6.68\times10^{-24}$ gm and for the scattering nucleus of gold we have $Z = 79$. Then :

$$r_{min} = \frac{zZe^2}{(\frac{1}{2})\,mv^2} = \frac{2\times79\times(4.8\times10^{-10})^2}{(\frac{1}{2})\,(6.68\times10^{-24})\times(1.6\times10^{9})^2}$$

$$= 4.59\times10^{-12}\text{ cm}$$

Thus we see that the nucleus has approximately a radius of the order of 10^{-12} cm.

1.5.4. Moseley introduces the idea of atomic number. We have seen above that the force that the nucleus of the scattering element exerts on the alpha particle depends on the magnitude of the nuclear charge, Z. However the first results obtained by this method were rather crude. Better and more accurate values were obtained by a young physicist Moseley in 1912.

Visible spectra of atoms usually arise when the most weakly bound atomic electrons are excited (atomic spectra). When a metal target is hit by a beam of high energy electrons, accelerated by a potential difference of about 10,000 volts, the atoms of the metal target are excited. Even some of the deep seated electrons are excited to higher energy levels and electrons from higher levels drop down to occupy the vacant positions. During such excitation radiant energy or X-rays are emitted. Moseley investigated the X-rays emitted by different elements. He determined the wavelengths (λ) of these X-rays by measuring the angle θ through which the rays are diffracted by a crystal of known interatomic spacing d, (usually potassium ferricyanide) and then making use of the well-known Bragg equation $n\lambda = 2d \sin \theta$. Moseley observed that each element emitted characteristic X-ray spectrum and the frequencies increased with increasing atomic weights. Moseley found that it was possible to fit all the characteristic highest frequencies by an empirical formula of the following type :

$$\nu = a(Z-b)^2$$

Here a is a constant ; b is called the screening constant and gives a measure of how far an electron is shielded from the nuclear charge by the other electrons. In order to gain an insight as to the identity of Z, Moseley plotted the square root of the reciprocal of the shortest observed wave-length $(1/\lambda)^{\frac{1}{2}}$ i.e the wave number, $(\nu)^{\frac{1}{2}}$, for each element against its atomic weight (Fig. 1.5). Although he thereby obtained a straight line a few points for some elements were off the line. He then plotted the square root of the wave numbers of the characteristic spectra of the elements against the order number or the serial number of the elements in the periodic table. This time he got a good straight line with all the points being on the line. The order number of an element in the periodic table is so significant that this order number was given the name *atomic number*. In the above relation between the frequency and Z, Moseley realised that Z correctly stood for the *nuclear charge* or the *atomic number* of the element concerned.

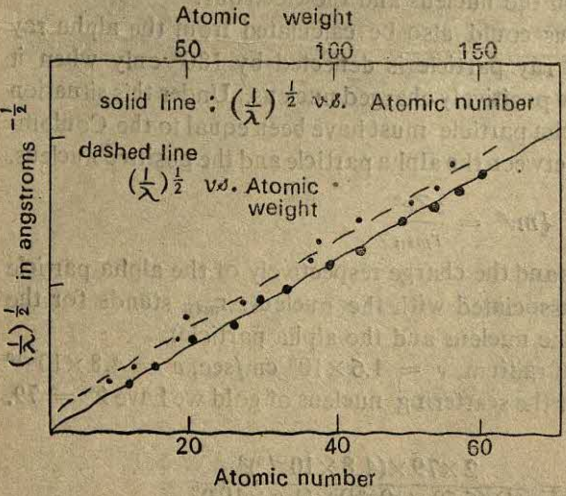

Fig 1.5. Moseley's data showing the relationship between wave number of X-ray spectra and atomic number/atomic weight of the elements

At this point it may be highlighted that the study of the X-ray spectra enabled to establish Z and thus the position of the element in the periodic table. These studies actually helped in sorting out the correct positions of the three pairs : Ni-Co, Ar-K, and Te-I in the periodic table. Originally placed in the periodic table on the basis of increasing atomic weights, their properties became inconsistent with their positions. However the inconsistencies were removed when the elements were arranged in the order of their atomic numbers. Thus atomic number is more fundamental than atomic weight.

It will be appropriate to elaborate the terms : frequency and wave number. Frequency, ν, indicates the number of waves passing a given point in unit time and is expressed as cycles per sec. Wave number, $\bar{\nu}$, the reciprocal of the wave length indicates the number of waves contained in one cm. The following relations hold good :

$$\lambda\nu = c\ ;\ \nu = \frac{c}{\lambda} = c\bar{\nu}\ ;\quad \therefore\ \bar{\nu} = \frac{\nu}{c}\ ;\ \nu = \frac{1}{\lambda}$$

1.5.5 Rutherford forecasts the existence of neutron. So far chemists have gathered informations on the nature of two fundamental particles, namely the electron and the proton. Electron is the unit of negative electricity and has negligible mass. The other particle is the proton of unit positive charge and of mass 1836 times heavier than the electron. In atomic mass unit (*amu*) the mass of the hydrogen atom is nearly 1. Rutherford now tried to analyse the composition of the nucleus of an atom. *Mass number* is defined as the integer nearest to the atomic weight of an element. Let us take the case of an element of mass number A and atomic number Z. Atomic number Z means that the nucleus of the element has Z protons which will contribute Z units of mass towards the atomic weight. In reality A is almost always much larger than Z. Rutherford now conjectured that there must be a third fundamental particle with a charge 0 and mass nearly equal to that of the proton. Existence of such a particle alone could explain the mass of an atom. Such a particle with charge 0 and mass 1 was named neutron.

1.5.6. Chadwick tracks down the neutron. Rutherford (1919) had already described another fantastic experiment of bringing about artificial transmutation of elements by hitting their nuclei by fast moving alpha particle. The very first reaction that startled the entire scientific world was the bombardment of nitrogen by alpha particle. Rutherford demonstrated that this reaction led to the birth of a new element oxygen :

$$\overset{14}{{}_7\text{N}} + \overset{4}{{}_2\text{He}} \rightarrow \overset{17}{{}_8\text{O}} + \overset{1}{{}_1\text{H}} \qquad (\overset{1}{{}_1\text{H}} = \text{proton})$$

In 1932 Chadwick bombarded very thin beryllium foil by fast moving alpha particles ejected from radioactive elements. This experiment led to the identification of a new fundamental particle which was not influenced by a magnetic or an electric field. Its mass was found to be the same as that of the proton. Consequently this new particle was the neutron, the existence of which had already been predicted by Rutherford. The reaction can be represented as :

$$\overset{9}{{}_4\text{Be}} + \overset{4}{{}_2\text{He}} \rightarrow \overset{12}{{}_6\text{C}} + \overset{1}{{}_0n}$$

Here the superscripts represent the mass numbers while the subscripts stand for the atomic numbers of the particles.

1.5.7. Synopsis of atomic structure. We now have three fundamental particles : electron, proton and the neutron. Taking the Rutherford model we now believe that the massive nucleus of an element is composed of the two fundamental particles : the proton and the neutron. These two together make up for the total mass of the element. Outside the very tiny nucleus are present the requisite number of the negatively charged electrons to make the atom electrically neutral. The number of protons in the nucleus correspond to the atomic number of the element. The difference between the mass number and the atomic number represents the number of the neutrons in the nucleus. Thus oxygen−16 has an atomic number 8. This means an atom of oxygen has 8 protons, 8 neutrons and 8 electrons. Oxygen −18 has the same atomic number as oxygen−16 and hence its atom is composed of 8 protons, 10 neutrons and 8 electrons. Species of the same element which differ only in their mass i.e. in the number of neutrons are called *isotopes* (*iso* means the same and *topos* means place).* Isotopes of the same element occupy the same position in the periodic table because their atomic number remains the same. Further examples of isotopes are : chlorine−35 and chlorine−37 ; carbon−12 and carbon−14 ; uranium−238 and uranium−235 ; hydrogen−1 and hydrogen −2 (also called by a special name deuterium).

We give below the charge and mass of the three fundamental particles :

Particle	Mass	Charge	
Electron	0.00548 *amu*	$-1e$	($e = 4.8 \times 10^{-10}$ esu)
Proton	1.00728 *amu*	$1e$	"
Neutron	1.00867 *amu*	0	

It needs to be explained what we understand by the term *atomic mass unit* (*amu*). One mole of carbon−12 contains one Avogadro number i.e. 6.023×10^{23} of atoms and weighs 12 gm. Therefore the weight of one atom of carbon−12 is (12/6.023) $\times\ 0^{-23}$ gm. But one atom of carbon−12 contains a total of 12 particles in the nucleus. Each particle in the nucleus is called a *nucleon*. Therefore *amu* should represent the mass of one nucleon in the carbon−12 scale. The *amu* is defined to be exactly $\frac{1}{12}$ of the mass of a carbon−12 atom.

$$1\ amu = (12/6.023) \times (1/12) \times 10^{-23}\ \text{gm} = 1.6603 \times 10^{-24}\ \text{gm}$$

(also note that 1 gm is equal to the Avogadro number expressed in *amu* i.e. 1 gm = 6.023×10^{23} *amu*).

At this point we will endeavour to dispel any confusion that might agitate the minds of young readers. In section 1.5.5 we have given the mass number of hydrogen as 1. The weight of one hydrogen atom in gm is 1.6736×10^{-24}. This is the lightest element known. This is made up of one proton and one electron. Since the electron has negligible mass the mass of the proton is also practically the same as that of the hydrogen atom. The mass of this lightest element is taken as 1 although the absolute mass is 1.6736×10^{-24} gm. Recall that charge of the electron has also been taken as −1 although the absolute value is 4.8×10^{-10} esu/electron.

Now that we have introduced the term *nucleon*, we can offer an alternative and more appealing definition of mass number. *Mass number represents the number of nucleons i.e. the total number of protons and neutrons in an element.*

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*Isotopes of an element have the same number of protons but different number of neutrons.

1.6. THE ARRANGEMENT OF THE EXTRANUCLEAR ELECTRONS

The Rutherford model of the atom was good enough so far as the nature of the nucleus and its relation to the extranuclear electrons was concerned. But it had a serious difficulty with regard to the motion of the electrons. A stationary electron is most likely to be drawn to the nucleus. Rutherford therefore proposed that the electrons were moving about the nucleus so that centrifugal force was balanced by the attractive force between the nucleus and the electrons. Electromagnetic laws predicted that if the electrons were in motion the atom should radiate energy until all electronic motion ceased. Bohr resolved this difficulty by making use of Planck's quantum theory of energy.

1.6.1. Planck's quantum theory. Experiments established that radiation from a heated body appeared only at certain definite frequencies. Planck assumed that a body cannot have any arbitrary energy but only certain permitted energy values. Light of frequency, ν, was thought to be radiated from the surface of the radiating body by a group of atoms oscillating with the same frequency. Thus he proposed :

$$E \propto \nu \; ; \quad \therefore E = h\nu$$

The above expression is known as Planck's quantum theory of radiation. It tells us that the energy emitted by a body is not continuous in nature but is in the form of discrete bundles or quanta. This quantum theory has been made use of by Bohr in analysing the spectrum of hydrogen atom. If an electron is to be excited from one quantised energy level to another it has to be supplied with an amount of energy which is equal to the difference between the two levels. On the other hand when an electron comes down from a higher energy level to a lower one energy equivalent to the difference between the two levels will be emitted.

The proportionality constant in the above equation is called Planck's constant and has a value of 6.27×10^{-27} erg-sec.

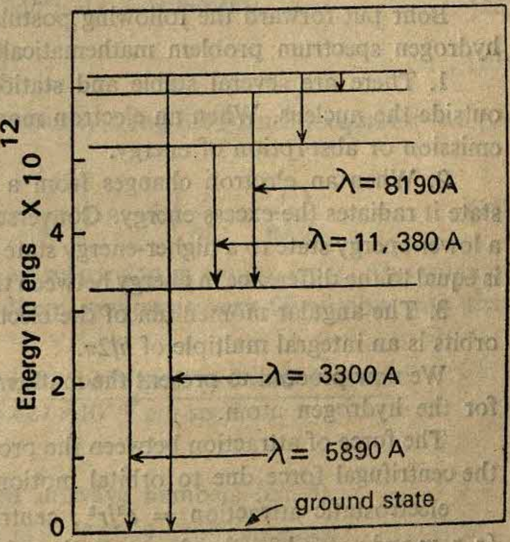


Fig. 1.6. Some transitions between electronic energy levels of the sodium atom.

In order to convince the young readers about the quantum nature of the electronic transitions we give in Fig 1.6 some transitions between electronic energy levels of the sodium atom. It is to be noted that no transitions are seen in between the transitions shown in the Figure. Thus we see that electronic transitions are quantised. ($E = h\nu$; $E = hc/\lambda$; so that the energy units will be erg. sec. cm. sec^{-1}. cm^{-1} i.e. ergs).

1.6.2. Rydberg analyses the hydrogen spectrum experimentally. Way back in 1889 Rydberg examined the spectrum of the hydrogen atom experimentally. He observed that the frequencies of the different spectral lines could be connected by the following empirical relation :

$$\nu = \text{a constant}\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right) = R\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right)$$

The constant R in the above relation is now known as the Rydberg constant. This equation remained a curiosity to physicists and chemists for quite a long time. It was after the contributions of great stalwarts like, Thomson, Rutherford, Planck and Bohr that a full appreciation of Rydberg's contribution to fundamental science became possible.

1.6.3. Niels Bohr explores the hydrogen spectrum theoretically. We have referred to the apparent contradiction between Rutherford's idea about the electron movement about the nucleus and the laws of electromagentics. According to the latter, if the electrons were in circular motion then they should radiate light until all electronic motion came to a halt. It was in 1913 that Niels Bohr proposed a detailed picture about the electron motion about the nucleus.

Bohr put forward the following postulates before he set about tackling the hydrogen spectrum problem mathematically :

1. There are several stable and stationary circular orbits for an electron outside the nucleus. When an electron moves in one of these orbits there is no emission or absorption of energy.

2. When an electron changes from a high-energy state to a lower-energy state it radiates the excess energy. Conversely when an electron is elevated from a lower-energy state to a higher-energy state it has to be fed with an energy which is equal to the difference in energy between these states.

3. The angular momentum of the electron during its motion in the circular orbits is an integral multiple of $h/2\pi$.

We now proceed to present the mathematical treatment of the Bohr's theory for the hydrogen atom.

The force of attraction between the proton and the single electron is equal to the centrifugal force due to orbital motion of the electron.

electrostatic attraction $= e^2/r^2$; centrifugal force $= mv^2/r$ . . . (1)

(e, r, m and v stand for the charge, radius of the orbit, mass and the velocity of the electron).

$$e^2/r^2 = mv^2/r \qquad \text{so that } mv^2r = e^2 \qquad \ldots (2)$$

The kinetic energy of the moving electron $= \frac{1}{2}mv^2$ . . . (3)

The potential energy due to attraction between the proton and the electron $= -e^2/r$ . . . (4)

The total energy of the hydrogen atom is given by the sum of the kinetic and potential energies : $E = \frac{1}{2}mv^2 + (-e^2/r)$ . . . (5)

From equation (2) $\frac{1}{2}mv^2 = \frac{1}{2}e^2/r$ so that the total energy of the hydrogen atom : $E = -\frac{1}{2}e^2/r$ . . . (6)

At this stage Bohr had to assume that the angular momentum of the electron would be multiples of $h/2\pi$. This would help to solve for the specific energies of the electron.

$mvr = nh/2\pi$ (n is any integer and h is Planck's constant) . . . (7)

Equation (6) indicates a solution of E provided we know r. Squaring the equation (7) we have : $m^2v^2r^2 = n^2h^2/4\pi^2$ . . . (8)

With the help of the equations (8) and (2) we can write :

$$m^2v^2r^2 = mv^2r.r.m = e^2rm = n^2h^2/4\pi^2 \qquad \text{. . . (9)}$$

Therefore $r = n^2h^2/4\pi^2e^2m$ . . . (10)

Putting the value of r in equation (6) we have :

$$E = -e^2/2(n^2h^2/4\pi^2e^2m) = -2\pi^2e^4m/n^2h^2 \qquad \text{. . . (11)}$$

Equation (11) has one variable in n. The equation thus tells us that the hydrogen atom can exist only at those energies permitted by integral values of the quantum number n.

Let us now examine the values of the energy emitted when the atom drops from an excited state II (corresponding to n_{II}) to a lower level I (corresponding to n_{I}). If E is the energy difference between the two states we have :

$$E = E_{\text{II}} - E_{\text{I}} = (-2\pi^2\, e^4m/n_{\text{II}}^2h^2) - (-2\pi^2e^4m/n_{\text{I}}^2h^2) \qquad \text{. . . (12)}$$

$$= 2\pi^2me^4/h^2\left(\frac{1}{n_{\text{I}}^2} - \frac{1}{n_{\text{II}}^2}\right) \qquad \text{. . . (13)}$$

Expressing this energy in terms of frequency using the Planck's equation we get at the following relation :

$$\nu = \frac{E}{h} = \frac{2\pi^2me^4}{h^3}\left(\frac{1}{n_{\text{I}}^2} - \frac{1}{n_{\text{II}}^2}\right) = R\left(\frac{1}{n_{\text{I}}^2} - \frac{1}{n_{\text{II}}^2}\right) \qquad \text{. . . (14)}$$

The R in equation (14) is the same R we referred to in section 1.6.2. The value of R obtained experimentally by Rydberg compares very favourably with that obtained by Bohr theoretically.

$$R = \frac{2\pi^2me^4}{h^3} = \frac{2(3.1416)^2\ (9.108\times10^{-28}\text{ gm})\ (4.8\times10^{-10}\text{ esu})^4}{(6.627\times10^{-27}\text{ erg-sec})^3}$$

$$= 3.2898\times10^{15}\text{ cycles/sec} = \nu$$

Rydberg constant is usually reported in wave numbers (cm^{-1}).

$$R = (\text{in } \bar{\nu}) = \frac{R(\text{in } \nu)}{c} = \frac{3.2898\times10^{15}\text{ cycles/sec}}{2.9979\times10^{10}\text{ cm/sec}}$$

$$= 109{,}737\text{ cm}^{-1}$$

The experimental value for the above constant as determined by Rydberg in 1889 was 109,677 cm^{-1}.

The Bohr manipulation gives us some clues to the size of the permitted circular orbits in terms of their radii. Equation (10) provides the radii of the orbits :

$$r = \frac{n^2h^2}{4\pi^2e^2m} = \frac{n^2(6.627\times10^{-27}\text{ erg-sec})^2}{4\times(3.1416)^2\times(9.108\times10^{-28}\text{ gm})\times(4.8\times10^{-10}\text{ esu})^2}$$

$$= n^2\times0.529\times10^{-8}\text{ cm} = 0.529\ n^2\text{ A (1A} = 10^{-8}\text{ cm)}$$

Thus we see that when n equals 1, the radius of the first orbit of the hydrogen atom i.e. the Bohr radius is 0.529 A symbolised as a_o. The radius of the second orbit ($n = 2$) will be four times the radius of the ground state orbit ($n = 1$). Similarly the radius of the third orbit will be nine times of the ground state radius.

The spectral lines corresponding to particular transitions in the hydrogen atom go by the name of their discoverers. Thus the transitions from the states $n = 2$ 3, 4 etc to the state $n = 1$ form the Lyman series. The transitions from the state $n = 3, 4, 5$ etc to the state $n = 2$ are known as the Balmer series. Transitions from the states $n > 3$ to the state $n = 3$ are called the Paschen series.

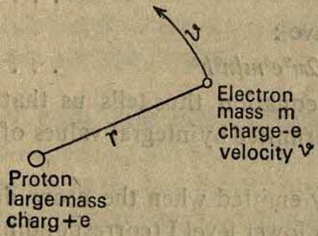


Fig. 1.7. Bohr's model of the hydrogen atom

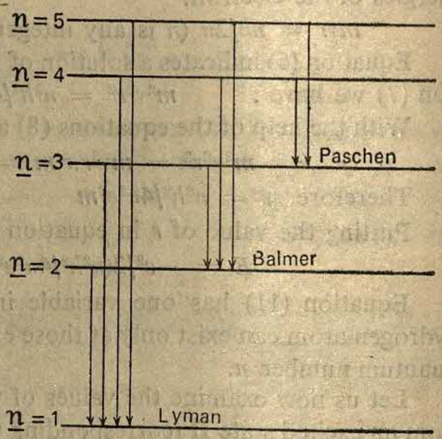


Fig. 1.8. Some of the transitions between energy states of the hydrogen atom.

We have treated above the hydrogen atom which has one proton ($Z = 1$) and one electron only. If we take the general case of an electron moving around a nucleus of charge + 2 (Z = 2) or of charge + 3 (Z = 3) (as in the case of He^+ or Li^{2+}) we have to replace the nuclear charge e by Ze in the above Bohr derivations. In that case

$E = -\frac{1}{2}Ze^2/r$ and substituting the value of r, $E = -\dfrac{2\pi^2mZ^2e^4}{n^2h^2}\left(r = \dfrac{n^2h^2}{4\pi^2mZe^2}\right)$

1.6.4. Sommerfeld adds to Bohr's ideas. Bohr's formula worked quite well for other one-electron systems like He^+ and Li^{2+}. But the theory ran into rough weather in multielectron atoms like He, Li or any species having more than one electron. Sommerfeld improved the situation somewhat by suggesting that orbits need not always have to be circular. Elliptical orbits are as well possible. Just as an ellipse requires two axes, elliptical orbits should also have two quantum numbers to describe them. Besides the principal quantum number, n, Sommerfeld proposed a second azimuthal quantum number, k, such that k can have values 1, 2, ... n. Later k was changed to l such that l could have the values 0.1, 2, ... $(n-1)$ i.e. l was put equal to $(k-1)$.

1.6.5. Different quantum numbers in multielectron systems. We have already seen in section 1.6.3. that the principal quantum number, n, primarily describes the energy and the size of the orbit.

$$E = -2\pi^2 e^4 m/n^2 h^2 = -\text{constant}/n^2 \; ; \; r = n^2 h^2/4\pi^2 e^2 m$$

In multielectron atoms the energy of each electron is dependent mostly on the value of the principal quantum number. With increase in the value of n the energy increases and so also the distance of the electron from the nucleus. The principal quantum number can have values 1, 2, 3, 4 etc but not 0. The orbits corresponding to n equal to 1, 2, 3, 4 are also known as K, L, M, N levels or shells.

Each level or shell of electrons carry one or more sublevels or subshells. The sublevels are indicated by the azimuthal quantum number or the orbital angular momentum quantum number, l. This quantum number usually provides an idea about the shape of the orbit. We have already seen for a particular n, the different values of l may be 0, 1, 2 . . . . . $(n - 1)$. Thus for a particular n, the number of values that l can assume is n. i.e there can exist n sublevels.

An electron with an orbital angular momentum quantum number may be thought of as an electric current moving in an orbit. A magnetic field is a natural consequence. In fact Zeeman had already demonstrated that atomic electrons are influenced by an applied magnetic field. Since this magnetic effect is connected with the angular momentum, the electron will have a magnetic quantum number, m_l. This quantum number, m_l, can assume $2l + 1$ values varying from $+ l$ to $- l$.

$$m_l = + l, (l-1), \ldots 0 \ldots -(l-1), -l$$

If l has a value 2, then m_l can have values $+ 2, +1, 0, -1, -2$.

Finally there is a fourth quantum number which is not interrelated with any of the above three quantum numbers. Each electron spins around its own axis. A charged particle spinning around its own axis behaves like a small magnet. The electron has only two spin quantum numbers, m_l, namely $+\frac{1}{2}$ and $-\frac{1}{2}$.

1.6.6. Pauli sets down the rules to assign quantum numbers to electrons. Now that we have as many as four different quantum numbers to describe the energy and size (principal quantum number), shape (azimuthal or orbital angular quantum number), orientation in space (magnetic quantum number) and the spin behaviour of the electron the question that arises is what is the rule that guides us to assign these quantum numbers to different electrons. Pauli has provided the answer in the form of his *exclusion principle*. Pauli exclusion principle runs as : *No two electrons in any atom can have the same set of four quantum numbers.* We can easily see that the Pauli principle has to be correct—otherwise all electrons will not be able to maintain their individual character ; some will be identical.

With the Pauli principle at our service our next question is : how many electrons can we have in a particular quantum level? When n is 1, l can only be 0. When l is 0, m_l can only be zero. But spin quantum number can still have two values. So two electrons can be accommodated in the level $n = 1$. Take the case of $n = 2$. Under this level there may be n sublevels with l equal to 0 and 1. When l is 0 the magnetic quantum number m_l can have $2l + 1$ further sublevels. These sublevels permitted by the magnetic quantum number were earlier called orbits but are now known as *orbitals*. Each of the two orbitals under $n = 2$ and $l = 0$ again can have two electrons. If we proceed this way we will see that the orbitals under $n = 2$ and $l = 1$ are as many as three $(2 \times 1 + 1 = 3)$. So these three orbitals can carry a total of six electrons. The final result for $n = 2$ is : we have a total of four orbitals and a total of eight electrons. It is also evident that for a given n the total number of electrons is given by $2n^2$. In Table 1.1 is given the allowed sets of the four quantum numbers for electrons.

Table 1.1. Allowed sets of Quantum Nunbers for Electrons

Level n	1	2				3								
Sublevel l	0	0	1			0	1			2				
Orbital m_l	0	0	+1	0	−1	0	+1	0	−1	+2	+1	0	−1	−2
Spin m_s $\uparrow = +\frac{1}{2}$; $\downarrow = -\frac{1}{2}$	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅

It is evident from Table 1.1 that for $n = 3$, five orbitals will exist with $l = 2$.

1.6.7. Symbols used for quantum levels and sublevels. We have already convinced ourselves that there cannot be any sublevel under $n = 1$ principal quantum number. There is thus only one orbital possible. This orbital is symbolised as $1s$. The s here is different from the spin quantum number symbol s. This s indicates that the orbital is spherically symmetrical. This is explained further in the next section. 1 in $1s$ stands for the principal quantum number 1. This orbital can have two electrons—one with up-spin and the other with down spin. The number of electrons in an orbital is indicated by appropriate superscripts. Thus for the $1s$ level we indicate one or two electrons by the following symbols :

$$1s^1 : \frac{\uparrow}{1s} ; \quad 1s^2 : \frac{\uparrow\downarrow}{1s}$$

For $n = 2$ we have an orbital with $n = 2$ and $l = 0$. This orbital is symbolised as $2s$. Note an s type orbital has $l = 0$. Then we have three orbitals under $n = 2$ and $l = 1$ because m_l can have three permitted values $+1$, 0, and -1. Orbitals with $l = 1$ are marked as p orbitals. Since the m_l values indicate merely the relative orientations in space, the three p orbitals are situated along the three cartesian axes x, y and z. So the three orbitals are marked as p_x, p_y and p_z. When the 2*s* and the three 2*p* levels are saturated by electrons we use the following expressions :

$$2s^2\,2p^6\;;\quad \underset{2s}{\underline{\uparrow\downarrow}}\quad \underset{2p_x}{\underline{\uparrow\downarrow}}\quad \underset{2p_y}{\underline{\uparrow\downarrow}}\quad \underset{2p_z}{\underline{\uparrow\downarrow}}$$

1.6.8. Wave character of electrons and electron orbitals. So far the electron has been treated on the model that it is a particle. The electron is so very tiny in nature that one could reasonably pose the question : can the electron behave as wave? The phenomena associated with wave behaviour are diffraction and interference. Davisson and Germer had demonstrated that electrons could be diffracted by crystals—thus proving that it has wave properties. Bohr made an attempt to explain away the duality of the particle and wave nature of the electron by proposing the *principle of complementarity*. He argued the same electron cannot behave as a particle and a wave simultaneously. It was at this stage that another luminary appeared on the scene. Werner Heisenberg proposed his *uncertainty principle:* it is not possible to specify at any given moment both the position and the momentum of the electron. It is most unlikely that the electron is moving from one point to another with a certain momentum at each point. It is safer to consider that the electron has a certain probability of being found at each point in space. The electron is so very tiny a particle that whatever technique we use in determining its position that will change its momentum by an unknown amount.

According to the Bohr's theory the radius of the 1*s* electron orbit is 0.529A i.e. the 1*s* electron always goes round the nucleus in a circular orbit of radius 0.529A. According to the uncertainty principle this cannot be the entire truth. It is true that the electron is most likely to be found along that circular orbit but it is also true that the electron may be found at other points around the nucleus. Schrodinger developed a wave equation which took into consideration the uncertainty as to its exact location and accommodated the probability concept. He provided us with the probability shapes of the different electrons around the nucleus. It is outside the scope of this elementary level book to go into how the shapes follow from Schrodinger's equation.

Orbits are fixed path along which electrons are assumed to move all the time. Orbitals, on the other hand, represent certain space about the nucleus, where the probability of finding a particular electron is very high. We describe below the shapes of the different orbitals originating from the different quantum numbers.

An *s* orbital is spherically symmetrical about the nucleus. It can easily be guessed that the chance of finding a negatively charged electron very close to the positively charged nucleus must be very low indeed. In fact the highest probability of finding the 1*s* electron is at a distance of 0.529A from the nucleus— thereafter the probability decreases. It is also of interest to note that for the 1*s* orbital l is 0 and so also m_l. So there is no directional character associated with the 1*s* orbital. Probability of finding this electron around the nucleus along all the three Cartesian axes is the same. It is therefore spherical in shape (Fig 1.9).

We have earlier seen that for $l = 1$, there are three m_l values $+1$, 0 and -1. Thus there are three *p* type orbitals. Since m_l quantum numbers indicate orientation in space it can be guessed that the three *p* orbitals will be directed along the three cartesian axes. These three orbitals are designated as p_x, p_y and p_z. Detailed mathematical analyses tell us that for each of the three *p* orbitals there are two dumb-bell shaped probability lobes on either side of a cartesian axis. There is equal probability of finding the electron on either side of the axis (Fig 1.9). There are five *d* orbitals. These originate from $l = 2$ whence m_l can have values $+2$, $+1, 0, -1$ and -2. The shapes of these orbitals are more complicated and we will not go into their discussion for the present.

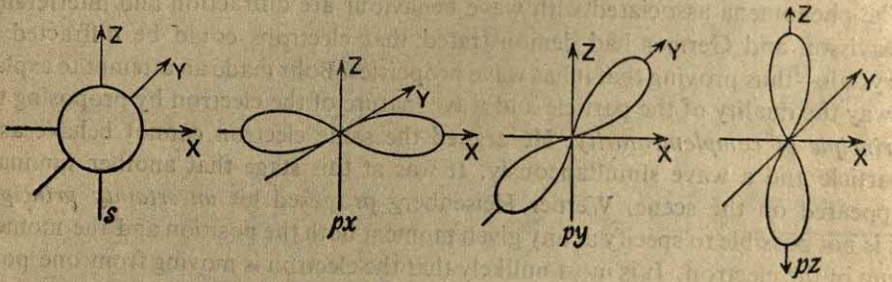


Fig. 1.9. Shapes of *s* p_x, p_y and p_z orbitals

1.6.9. Relative energies of the different orbitals and their stability. The higher the energy the lower is the stability of the orbital. The following general considerations will be in order.

1. As the value of the principal quantum number, *n*, increases the energy of the orbitals also increases i.e. the energy of $n = 2$ orbitals is greater than the energy of the $n = 1$ orbital.

2. Under the same *n*, the energy of the orbitals increases with increasing *l* value i.e the energy of 2*p* ($l = 1$) orbitals is greater than that of the 2*s* orbital : $2p > 2s$; $3d > 3p > 3s$.

3. For the same *n* and a particular *l* only m_l values can change. Variation in the m_l values gives orbitals which differ in their relative orientation in space. Thus the p_x, p_y and p_z orbitals under $n = 2$ or $n = 3$ or any higher *n* will have the same energy : $2p_x = 2p_y = 2p_z$; $3p_x = 3p_y = 3p_z$ etc.

Energies of orbitals on the hydrogenic model (i.e one proton and one electron in different orbitals) have been calculated. The following order has been found :

$$1s < 2s < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f$$

$$\xrightarrow{\hspace{12cm}}$$

Energies of the orbitals increase ; stability of the orbitals decreases.

It is to be particularly noted that the orders : $4s < 3d$; $5s < 4d$; $6s < 5d$ are contrary to our expectation. The explanation lies in the fact that the relevant *s* orbitals are little more penetrating i.e. they move a little closer to the nucleus and thus see more of the nuclear charge than the *d* orbitals. Electrostatic attraction of the nucleus increases the stability of these *s* orbitals to some extent.

1.6.10. Electron building-up process. The following rules are to be followed in the electron building-up process in multielectron atoms :

1. Lower energy orbitals will be filled up first. Electrons wlll move up to higher energy orbitals only after the filling up of the lower energy orbitals is complete.

2. In order to avoid interelectronic repulsion electrons will not tend to share orbitals i.e. they will not normally like to pair their spins in the same orbital.

3. Electrons will share one orbital only when orbitals of similar energy are not available.

Making use of the above three rules we can write out the electron distributions of the following elements from hydrogen (atomic number 1) to neon (atomic number 10) (Table 1.2).

Table 1.2. Electron Distribution of Elements Hydrogen to Neon

Element	Atomic number	Electronic symbol	Distribution of electrons in orbitals				
Hydrogen	1	$1s^1$	$\overset{\uparrow}{1s}$				
Helium	2	$1s^2$	$\overset{\uparrow\downarrow}{1s}$				
Lithium	3	$1s^2 2s^1$	$\overset{\uparrow\downarrow}{1s}$	$\overset{\uparrow}{2s}$			
Beryllium	4	$1s^2 2s^2$	$\overset{\uparrow\downarrow}{1s}$	$\overset{\uparrow\downarrow}{2s}$			
Boron	5	$1s^2 2s^2 2p^1$	$\overset{\uparrow\downarrow}{1s}$	$\overset{\uparrow\downarrow}{2s}$	$\overset{\uparrow}{2p}$		
Carbon	6	$1s^2 2s^2 2p^2$	$\overset{\uparrow\downarrow}{1s}$	$\overset{\uparrow\downarrow}{2s}$	$\overset{\uparrow}{2p}$	$\overset{\uparrow}{2p}$	
Nitrogen	7	$1s^2 2s^2 2p^3$	$\overset{\uparrow\downarrow}{1s}$	$\overset{\uparrow\downarrow}{2s}$	$\overset{\uparrow}{2p}$	$\overset{\uparrow}{2p}$	$\overset{\uparrow}{2p}$
Oxygen	8	$1s^2 2s^2 2p^4$	$\overset{\uparrow\downarrow}{1s}$	$\overset{\uparrow\downarrow}{2s}$	$\overset{\uparrow\downarrow}{2p}$	$\overset{\uparrow}{2p}$	$\overset{\uparrow}{2p}$
Fluorine	9	$1s^2 2s^2 2p^5$	$\overset{\uparrow\downarrow}{1s}$	$\overset{\uparrow\downarrow}{2s}$	$\overset{\uparrow\downarrow}{2p}$	$\overset{\uparrow\downarrow}{2p}$	$\overset{\uparrow}{2p}$
Neon	10	$1s^2 2s^2 2p^6$	$\overset{\uparrow\downarrow}{1s}$	$\overset{\uparrow\downarrow}{2s}$	$\overset{\uparrow\downarrow}{2p}$	$\overset{\uparrow\downarrow}{2p}$	$\overset{\uparrow\downarrow}{2p}$

1.7. REPRESENTATIVE ELEMENTS AND TRANSITION ELEMENTS

The elements cited in Table 1.2 strictly follow the rules of electron building up process enumerated above. This filling up of electronic levels according to rules continue upto the element argon (Ar) of atomic number 18. Upto argon the sub-levels (1*s* to 3*p*) are all filled. Thereafter filling up of the 3*d* should have started. But we have seen that there is a reversal in the energy order at this stage : $4s < 3d$. Therefore in potassium (atomic number 19) and calcium (atomic number 20) the

15661

4*s* sublevel is filled up. In the next ten elements from scandium(atomic number21) to zinc (atomic number 30) the 3*d* sublevel is gradually filled up. Some special stability is attained when any electron sublevel is either half-filled or completely filled. Thus we see that in chromium and copper the atomic ground state electronic arrangements have respectively five and ten electrons in the 3*d* sublevel and consequently both have only one electron in the 4*s* sublevel (Table 1.3).

At this stage we can introduce the definitions of *representative elements and transition elements. Representative elements have their d levels either entirely empty or completely filled in their ground atomic states and in their oxidation states. Transition elements have their d sublevel incompletely filled either in their ground state or any of their oxidation states.* This definition excludes zinc from the first series transition elements because both in the atomic state and in the only oxidation state, namely +2, the metal has a saturated 3*d* sublevel.

We would like to refer to the way electrons are lost from the transition elements during chemical reactions. Since the 4*s* sublevel is little more stable than the 3*d* sublevel one would expect that during chemical reaction electrons from the 3*d* sublevel participate in preference to the 4*s* electrons. Because of several factors like shielding effects of 3*d* and 4*s* electrons, nuclear charge and penetrating character of the different electrons it is a reality that to start with the 4*s* electrons are stabler than the 3*d* electrons. After the addition of a few electrons in the 3*d* sublevel the 3*d* electrons gain in stability. So in chemical reactions the 4*s* electrons are lost first and then the 3*d* electrons.

Two other transition series elements are known :

Second series : Yttrium (atomic number 39) to Silver (atomic number 47). These elements have incompletely filled 4*d* sublevel.

Table 1.3. Electron Distribution of First Series Transition Elements*

Element	Atomic Number	Electronic Symbol	Distribution of Electrons in Orbitals
Sc	21	$1s^22s^22p^63s^23p^64s^23d^1$	$[\mathrm{Ar}]\underset{4s}{\uparrow\downarrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\_}\ \underset{3d}{\_}\ \underset{3d}{\_}\ \underset{3d}{\_}$
Ti	22	$1s^22s^22p^63s^23p^64s^23d^2$	$[\mathrm{Ar}]\underset{4s}{\uparrow\downarrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\_}\ \underset{3d}{\_}\ \underset{3d}{\_}$
V	23	$1s^22s^22p^63s^23p^64s^23d^3$	$[\mathrm{Ar}]\underset{4s}{\uparrow\downarrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\_}\ \underset{3d}{\_}$
Cr	24	$1s^22s^22p^63s^23p^64s^13d^5$	$[\mathrm{Ar}]\underset{4s}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}$
Mn	25	$1s^22s^22p^63s^23p^64s^23d^5$	$[\mathrm{Ar}]\underset{4s}{\uparrow\downarrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}$
Fe	26	$1s^22s^22p^63s^23p^64s^23d^6$	$[\mathrm{Ar}]\underset{4s}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow}\ \underset{dd}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}$
Co	27	$1s^22s^22p^63s^23p^64s^23d^7$	$[\mathrm{Ar}]\underset{4s}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}$

Ni	28	$1s^22s^22p^63s^23p^64s^23d^8$	$[\mathrm{Ar}]\underset{4s}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow}\ \underset{3d}{\uparrow}$
Cu	29	$1s^22s^22p^63s^23p^64s^13d^{10}$	$[\mathrm{Ar}]\underset{4s}{\uparrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}$
Zn	30	$1s^22s^22p^63s^23p^64s^23d^{10}$	$[\mathrm{Ar}]\underset{4s}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}\ \underset{3d}{\uparrow\downarrow}$

* [Ar] represents the distribution of the first eighteen electrons correponding to the argon atom.

Third series : Hafnium (atomic number 72) to Gold (atomic number 79). These elements have incompletely filled 5*d* sublevel.

1.8. THE INNER TRANSITION ELEMENTS

In the periodic table there are two series of elements which have their inner 4*f* or 5*f* sublevel incompletely filled in their ground state or in any of their oxidation state. These elements are named *inner transition elements*. The 4*f* or the 5*f* sublevel is protected by two other higher sublevels : 4*f* is covered by 5*s* and 5*p* while the 5*f* is guarded by the 6*d* and 7*s* sublevels.

First series of inner transition elements : These are the lanthanides or the rare earths. There are fourteen of them after lanthanum. Table 1.4 gives their atomic number, name and symbol.

Table 1.4. The Lanthanides

Atomic Number	Element	Symbol	Atomic Number	Element	Symbol
57	Lanthanum	La	65	Terbium	Tb
58	Cerium	Ce	66	Dysprosium	Dy
59	Praseodymium	Pr	67	Holmium	Ho
60	Neodymium	Nd			
61	Promethium	Pm	68	Erbium	Eb
62	Samarium	Sm	69	Thullium	Tm
63	Europium	Eu	70	Ytterbium	Yb
64	Gadolinium	Gd	71	Lutecium	Lu

The 4*f* sublevel has a total electron accommodation capacity of 14. After lanthanum these 14 electrons are added one by one to the 14 elements from cerium to lutecium. Some electron distributions are given below :

La^{3+} ;	At. No.	57 ;	[Pd]	$4f^0$	$5s^2$	$5p^6$
Ce^{3+} ;	,,	58 ;	[Pd]	$4f^1$	$5s^2$	$5p^6$
Gd^{3+} ;	,,	64 ;	[Pd]	$4f^7$	$5s^2$	$5p^6$
Tm^{3+} ;	,,	69 ;	[Pd]	$4f^{12}$	$5s^2$	$5p^6$
Yb^{3+} ;	,,	70 ;	[Pd]	$4f^{13}$	$5s^2$	$5p^6$
Lu^{3+} ;	,,	71 ;	[Pd]	$4f^{14}$	$5s^2$	$5p^6$

There is an interesting difference between the regular transition series elements (such as manganese, nickel or copper) and the inner transition series elements. In the regular transition series elements the incompletely filled *d* sublevel is just below the next *s* sublevel. As a result after the two *s* electrons are gone the *d* electrons become quite vulnerable to attack by chemical reagents. Depending on the efficacy of the reagents employed one or more electrons may be withdrawn from the *d* level for valence purposes. We thus see variable valence is a common feature of the chemistry of the regular transition elements eg : manganese exhibits valences 0, 1, 2, 3, 4, 5, 6 and 7 ; nickel shows 0, 1, 2, 3 and 4 ; copper gives 1, 2 and 3. But the lanthanides have their 4*f* sublevel firmly protected by the two higher energy sublevels 5*s* and 5*p*. The consequence is that normally the deep-seated 4*f* electrons cannot be utilised for valence purposes. In the lanthanides variable valence is therefore not a common feature.

Second series of inner transition series elements : These are the actinides, beginning with actinium (Ac ; atomic number 89) and ending till now in lawrencium (Lw ; atomic number 103). The general electron distribution of the elements may be represented as :

$$[\mathrm{Rn}]\ 5f^{n}\ 6d^{2/1}\ 7s^{2} \qquad \text{or} \qquad [\mathrm{Rn}]\ 5f^{n+2/1}\ 7s^{2}$$

The following are the elements coming after actinium :

Atomic number	Element	Symbol	Atomic number	Element	Symbol
90	Thorium	Th	91	Protactinium	Pa
92	Uranium	U	93	Neptunium	Np
94	Plutonium	Pu	95	Americium	Am
96	Curium	Cm	97	Berkelium	Bk
98	Californium	Cf	99	Einsteinium	Es
100	Fermium	Fm	101	Mendeleevium	Md
102	Nobelium	No	103	Lawrencium	Lw

EXERCISES

1. Name the fundamental particles and describe their characteristics.

2. Describe how it was established that electron is a negatively charged particle. How did Thomson determine the charge/mass ratio of the electron?

3. What do you understand by *mole of electrons*? What is the total charge associated with a *mole of electrons*? Hence deduce the charge carried by a single electron.

4. Does the mass of an electron depend on its speed? What is the meaning of rest mass of an electron?

5. Distinguish between electron orbit and orbital.

6. Name the element of atomic number 10 and explain its electron distribution.

7. Give all the four quantum numbers of the last two electrons of neon and hence explain Pauli exclusion principle.

8. Describe Rutherford's experiment that led to his proposing the nuclear model of the atom.

9. In what respects isotopes of an element vary? Explain with respect to hydrogen, chlorine, oxygen and carbon.

10. Why is it that isotopes of an element exhibit similar chemical properties? In what respects do you expect them to show some variation in properties?

11. Distinguish between representative elements and transition elements.

12. What is the maximum number of 4*f* electrons in an atom? Name the first series of elements in which we find *f* electrons.

13. An electron has the quantum numbers 3, 2, 1 and $-\frac{1}{2}$. What are the symbols used for these quantum numbers?

14. What happens to the energy and the stability of the hydrogen electron as its orbit radius is increased?

15. It is experimentally observed that the the energy required to lift the hydrogen electron from $n = 1$ to $n = 2$ is 235 KCal/mole while that for lifting it from $n = 4$ to $n = 5$ is only 7 KCal/mole. How do you proceed to explain this?

16. How many electrons can there be with $n = 3$ and $l = 2$? What will be the total number of electrons with $n = 3$?

CHAPTER 2

RADIOACTIVITY

2.1. DISCOVERY : MOTHER NATURE LENDS A HAND

Towards the fag end of the nineteenth century (1896) some experiments were under way in Paris which were destined to change the face of science in a big way. Three immortal figures Becquerel, Marie and Pierre Curie participated in these epoch making scientific studies. Alongside these three giants was Mother Nature who, too, offered a helping hand to three of her great favourites. It was then believed that potassium uranyl sulphate, a double salt of potassium sulphate and uranyl sulphate K_2SO_4. UO_2SO_4 was a fluorescent chemical. A fluorescent substance absorbs energy of a particular frequency from an exciting source and after the source of excitation is removed it emits radiations of a different frequency. Becquerel observed that flourescence is shown by potassium uranyl sulphate after exposure to X-rays. He then decided to examine if fluorescence could be observed in the above material after exposure to sunlight. A sample of the double salt was prepared for exposure to sunrays. It was here that Nature decided to step in so that a scientific discovery of far-reaching effect on human civilisation could be made. For several days in the month of February, 1896, the sky over Paris was overcast. Becquerel felt frustrated but lived upto his standing as a scientist of the very first order. Instead of throwing away the sample he exposed the sample to photograhic plate and on development of the exposed plate he was amazed to see that there was good evidence of emission of radiation from the uranyl compound. The same effect was also observed when the compound was wrapped in black paper for quite some time and then exposed to photographic plate. Becquerel therefore made a startling conclusion : *uranyl compounds spontaneously emit radiation.* He realised that a breakthrough in fundamental science was in the offing and it was the time for bright young people gifted with talent, devotion and perseverence to move in. In came young Pierre Curie who had already established himself as a fine experimentalist, and another unassuming young lady from Poland. She was Marie Sklodovoska. The trio then started analysing uranium minerals one after another for their uranium content as also the radioactivity. It was in the mineral pitchblende that they bumped upon an amazing observation that the radioactivity far exceeded its uranium content. At this point young Marie suggested that pitcblende must be carrying a new element which was more radioactive than uranium. Intense activity followed and afterwards it was possible to isolate a new element which indeed was far more radioactive than uranium. In order to immortalise the advent of a gifted lady in the arena of science and also to show honour to her motherland Poland the new element was named polonium. Within a shortwhile another new radioactive element called radium was isolated from pitchblende. All these brilliant researches were recognised when the trio was awarded the Nobel Prize for physics in 1903. It was also the year that Marie Sklodovoska, later Curie, received her Doctorate from Sorbone.

The phenomenon of spontaneous emission of radiation from the interior of an element is known as radioactivity.

2.2. A LOOK AT THE NATURE OF RADIOACTIVITY

In the early days of the development of the subject studies were confined to naturally occurring radioelements like uranium, thorium, radium, polonium etc. Spontaneous disintegration of the nucleus led to emission of radiations. The rate of disintegration and the nature of the radiation were characteristic of each radioelement. Three different types of radiation were found in naturally occurring radioactive elements. These are : (1) alpha rays (α) (2) beta rays (β) and (3) gamma rays(γ). With the passage of time induced or artificial radioactivity was discovered. Studies on artificial radioactivity revealed that positrons (positive counterpart of the electron) and neutrons may also appear as radiations due to the disintegration of the nuclei of these artificially radioactive elements. It is to be noted that in the case of natural radioactive elements all the three radiations, alpha, beta and gamma, are not emitted simultaneously. While alpha and beta rays have particle nature, gamma rays have wave nature. Gamma rays often accompany alpha and beta emissions to relieve the product nuclei of the excess energy it might have.

2.2.1. The nature of the alpha rays (α). Rutherford conclusively demonstrated that the alpha particles are doubly charged helium ions i.e. helium atom minus two electrons. He first determined the charge to mass ratio (e/m) of the alpha particles from different radioelements. The technique employed was the one developed by Thomson for the measurement of (e/m) of the cathode rays. In all the cases Rutherford found that the (e/m) of the alpha particles was the same, namely $14.4. \times 10^{13}$ esu/gm. The (e/m) of protons was about 28×10^{13} esu/gm. So the (e/m) of the alpha particles was just half that of the proton. This could mean two things : (1) if the charge of the alpha particles were $+1$ the mass must be double that of the proton i.e 2 or (2) if the charge of the alpha particles were $+2$ then the mass must be 4. An independent determination of the charge was called for. Alpha rays were allowed to pass through an aperture of known area on to a plate connected to an electrometer to measure the charge. The alpha particles were passed through a magnetic field to deflect away any accompanying beta particle or electron produced through ionisation caused by the alpha rays. Thereafter with the help of a light sensitive ZnS screen and a microscope the number of alpha particles produced inside a small tube were counted. Thus the charge accumulated by the electrometer per unit time and also the number of the alpha particles produced per unit time were known. The charge per alpha particle could then be calculated. The value thus obtained was 9.3×10^{-10} esu/alpha particle. This value was double the value for a single electron, 4.8×10^{-10} esu/electron.

Thus it was conclusively proved that the mass of the alpha rays was 4 i.e. four times that of the proton.

It was demonstrated by examining the behaviour of these rays in applied electric and magnetic fields that these rays were positively charged. In the meantime Ramsay and Soddy had been looking for helium. They observed that helium could be found in the radioactive radiations emanating from radium and other radioactive substances. That there must be a connection between alpha particles and doubly charged helium ions was finally convincingly demonstrated by Rutherford. He planned to enclose some alpha ray emitting radioelement in a thin walled tube such that the alpha rays could penetrate through the tube into an outer tube connected to a spectrum tube. On examining the spectrum it could be decided whether or not the gas involved was really helium.

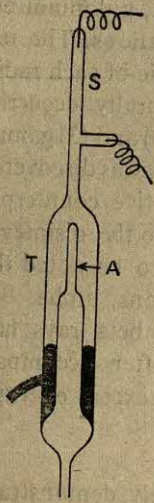


Fig. 2.1. Apparatus for detection of helium in alpha rays

Rutherford put in some radon gas, a known alpha emitter, into the thin walled tube A (Fig 2.1). The tube A was sealed to an outer tube T provided with a sidetube through which mercury could be pushed in. The tube T was connected to a spectrum tube S provided with two electrodes. At the beginning of the experiment the outer tube was partially evacuated. After a few days of putting in the radon gas in the inner tube A the mercury level was raised to force the gas accumulated in the tube T to the spectrum tube S. On the passage of an electric discharge the gas gave out a spectrum which was the same as that of helium gas. In a control experiment it was also demonstrated that no helium gas accumulated in the tube T when the inner tube A was filled with helium. Thus it were the alpha paricles that could penetrate the thin walled tube A and not helium gas.

The velocity of the alpha particles usually varies in and around 2×10^9 cm/sec i.e. around one-fifteenth of the velocity of light. It is a massive particle with significant velocity. Its high kinetic energy gives it a high ionising power i.e. it can effectively knock off electrons from air or any gas.

2.2.2. The nature of the beta rays (β). The identity of the beta rays with electrons was established from measurements of *(e/m)* with the help of Thomson's apparatus. The *(e/m)* was found to have a value of around 5.274×10^{17} esu/gm ; 1.77×10^8 coulomb/gm. in good agreement with that found for electrons. Deflection of the beta rays in an electric field also showed that these were negatively charged particles. Since the mass of these rays is quite negligible compared to that of the alpha

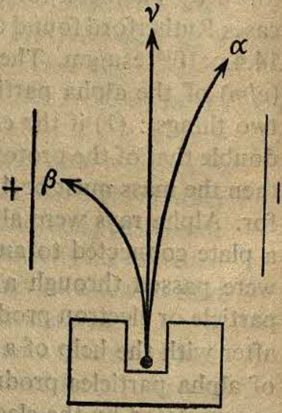


Fig. 2.2. Deflection of the three different rays from naturally radioactive elements in an electrc field,

particles, their kinetic energy is less and hence the ionising power is less than the alpha rays. Understandably, however, penetrating power of the beta particles is greater than that of the alpha particles. Velocity of these particles compares with that of light (about 2×10^{10} cm/sec). It may be pointed out here that the velocity often changes considerably depending on the source (cf section 1.3.4 : Chapter 1).

2.2.3. The nature of the gamma rays (γ). When a radioactive element emits an alpha particle or a beta particle the resulting daughter element is often produced in an excited state. The daughter element nucleus releases this excitation energy in the form of gamma ray. Gamma rays are radiations of extremely short wave length i.e. high frequency. These have no particle character and are not deflected either way in an electric or magnetic field. Gamma rays therefore have no mass or charge. Table 2.1 presents a comparative evaluation of the properties of the three types of radiations from natural radioelements.

Table 2.2. Properties of alpha, beta and gamma rays

	Alpha rays (α)	Beta rays (β)	Gamma rays (γ)
Nature	Particle	Particle	Wave
Electrical Character	Positively charged	Negatively charged	Neutral
Response to magnetic field	bends slightly	bends considerably opposite to the direction of alpha rays	Neutral
Charge/mass	14.4×10^{13} esu/gm	5.274×10^{17} esu/gm	—
Charge	$+9.3 \times 10^{-10}$ esu	-4.8×10^{-10} esu	0
Mass	4	1/1836 of hydrogen atom	0
Velocity	$\sim 2 \times 10^{9}$ cm/sec	$\sim 2 \times 10^{10}$ cm/sec	$\sim 3 \times 10^{10}$cm/sec
Ionising power	very high	less	nil
Penetrating power	low	greater than alpha	quite high

2.3. RADIOACTIVITY — A NUCLEAR PHENOMENON

Radioactivity orginates in the nucleus of an atom. The following points will convince us that radioactivity is a nuclear phenomenon.

1. Alpha particle is massive ; it carries a mass 4 and a charge + 2. Ejection of such a particle is possible from within the nucleus alone since extranuclear part consists of negatively charged particles of negligible mass.

2. Beta particles are basically electrons. But these cannot be the extranuclear electrons. Loss of extranuclear electrons can give rise to cations of the same element but ejection of beta particle leads to the formation of an element with

an entirely new set of properties. It is only possible if the beta particle comes from within the nucleus of the atom. Moreover the velocity (2×10^{10} cm/sec) of the beta particles is nearly ten times that of the cathode rays which are also electrons. This also means that the beta particles are ejected from within the nucleus with a tremendous velocity.

3. Radioactivity is spontaneous and remains independent of temperature, pressure and other conditions. A radioactive element shows the same amount of activity whether it is in elementary state or in the form of a compound. This too points to the fact that it is a nuclear phenomenon.

4. Radioactivity leads to the formation of a new element with an entirely new set of properties different from those of the mother. This can only happen when there is a change of atomic number—which again is possible on transformation of the nucleus.

2.4. RADIOACTIVITY AND CHEMICAL REACTION

1. A chemical reaction occurs as a result of interaction of the outermost shell electrons i.e. valence electrons of the combining elements. No change in atomic number of the element can occur as a result of any chemical reaction. But the most fundamental change that occurs on the ejection of an alpha particle or a beta particle is the change in atomic number of the radioelement.

2. Chemical reactions are often reversible and are influenced by external conditions like pressure, temperature, volume and concentration. But radioactivity is irreversible and cannot be influenced by any external conditions.

3. Radioactive disintegrations are spontaneous and need no activation energy. Chemical reactions need activation energy.

4. Radioactive disintegrations liberate much larger amount of heat than chemical reactions.

2.5. CHANGES IN THE NUCLEUS DUE TO RADIOACTIVITY

2.5.1. Change due to ejection of an alpha particle. We have already seen that an alpha particle is a doubly charged helium ion. When such a particle is ejected from within the nucleus the mass of the resulting element will decrease by 4 units and atomic number by two units. (Recall that the helium nucleus is composed of two neutrons and two protons—giving a mass of 4 and atomic number 2). The daughter element therefore is shifted two places to the left in the periodic table.

$$ {}^{238}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{234}_{90}\mathrm{Th} \; ; \quad {}^{226}_{88}\mathrm{Ra} \rightarrow {}^{222}_{86}\mathrm{Rn} + {}^{4}_{2}\mathrm{He} \quad ({}^{4}_{2}\mathrm{He} = \alpha) $$

2.5.2. Change due to ejection of a beta particle. A beta particle is a fast moving electron that comes out of the nucleus. The nucleus itself does not have any beta particle. Ejection of a beta particle is preceded by the transformation of a neutron into a proton and an electron. The beta particle is ejected but the newly created proton remains. As a consequence the atomic number of the resulting element goes up by one but the mass remains the same since the beta particle has negligible mass. The daughter element therefore is shifted one place to the right of the periodic table.

$$ {}^{1}_{0}n \rightarrow {}^{1}_{1}\mathrm{H} + {}^{0}_{-1}e \ ; \quad {}^{234}_{90}\mathrm{Th} \rightarrow {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}e \quad ({}^{0}_{-1}e = \beta) $$

$$ ({}^{1}_{1}\mathrm{H} = \text{proton}) \qquad {}^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}e $$

2.5.3. Change due to ejection of gamma ray. We have noted that gamma ray is a radiation and often follows the ejection of an alpha or a beta particle. The nucleus of the daughter element most often remains in an excited state. The excitation energy is liberated in the form of gamma ray. Since gamma ray has no mass or charge there occurs no change in the mass or the atomic number of the radioelement. The nucleus merely goes to a stabler form.

2.6. RADIOACTIVE DISINTEGRATION SERIES

Spontaneous disintegration leads to the formation of a new element. If this new element is also radioactive it will also break down to give birth to another element. Such a process of disintegration will continue till the product nucleus is a stable one. We will later see that the ratio of neutron to proton in the nucleus is the root factor that causes radioactivity. Spontaneous disintegration of a natural radioelement will continue till there is a stable ratio of neutron to proton in the nucleus. The isotopes constituting such a disintegration process form a *radioactive disintegration series.*

There are three naturally occurring disintegration series. One such series beginning in uranium—238 and ending in lead—206 is depicted in Table 2.3. It should be noted that all the three disintegration series end in isotopes of lead. Lead is closest to the natural radioelements and some of its isotopes (*but not all*) are non-radioactive.

Table 2.3. Uranium-238 disintegration series

$$\begin{tikzcd}
{}^{238}_{92}\mathrm{U} \arrow[r, "\text{Alpha}"] & {}^{234}_{90}\mathrm{Th} \arrow[r, "\text{beta}"] & {}^{234}_{91}\mathrm{Pa} \arrow[r, "\text{beta}"] & {}^{234}_{92}\mathrm{U} \arrow[d, "\text{alpha}"] \\
{}^{218}_{84}\mathrm{Po} \arrow[d, "\text{alpha}"'] & {}^{222}_{86}\mathrm{Rn} \arrow[l, "\text{Alpha}"'] & {}^{226}_{88}\mathrm{Ra} \arrow[l, "\text{Alpha}"'] & {}^{230}_{90}\mathrm{Th} \arrow[l, "\text{Alpha}"'] \\
{}^{214}_{82}\mathrm{Pb} \arrow[r, "\text{beta}"] & {}^{214}_{83}\mathrm{Bi} \arrow[r, "\text{beta}"] & {}^{214}_{84}\mathrm{Po} \arrow[r, "\text{alpha}"] & {}^{210}_{82}\mathrm{Pb} \arrow[d, "\text{beta}"] \\
 & {}^{206}_{82}\mathrm{Pb} & {}^{210}_{84}\mathrm{Po} \arrow[l, "\text{alpha}"'] & {}^{210}_{83}\mathrm{Bi} \arrow[l, "\text{beta}"']
\end{tikzcd}$$

2.7. HOW DO WE REPRESENT NUCLEAR REACTIONS?

In nuclear reactions mass balance and atomic number balance are shown. Since gamma rays do not change the mass or the atomic number these are not shown in writing nuclear reactions.

2.8. GROUP DISPLACEMENT LAW

As the subject of radioactivity started growing lots of species were identified, which resulted from the emission of alpha particle or beta particle. Some of these species were found to have the same properties but varied in their mass. Since emission of an alpha particle resulted in a loss of 2 units of atomic number and 4 units of mass, the resulting daughter should go to two places to the left of its mother in the periodic table. On the other hand emission of a beta particle increases the atomic number by one unit and hence the daughter should be shifted one position to the right of its mother. Fajans and Soddy proposed their group displacement law as under :

Alpha emission will shift the daughter to two groups to the left of the mother while beta emission will shift the daughter to one group to the right of the mother. One alpha emission followed by two consecutive beta emissions will give a product which will occupy the same place as the original mother in the periodic table.

The above group displacement law carried the clue to our ideas about *isotopes.* One alpha emission and then two consecutive beta emissions produce two species which have the same atomic number and the same position in the periodic table. These are called isotopes. Several definitions of isotopes may be advanced :

1. Isotopes are species which have the same atomic number but different mass number.
2. Isotopes are species of the same element which differ in their atomic weights.
3. Isotopes are species which have the same number of protons but different number of neutrons.

While talking of isotopes the young readers are reminded that chemical properties are the dictates of atomic number. Since isotopes possess the same atomic number they will show the same chemical properties. Some physical properties which are mass-dependent only vary.

2.9. LET'S TAKE A LOOK INTO THE STABILITY OF THE NUCLEI

The question that may agitate the minds of young readers is : why do some nuclei break down at all? The answer must lie in an inspection of the components of the nuclei i.e. in the number of the neutrons and protons. The frequency of occurrence of stable nuclei alongwith their mass number (*A*), number of neutrons (*N*) and number of protons (*Z*) is shown in Table 2.4.

Table 2.4. Frequency of occurrence of stable nuclear types

A (mass number)	*N* (neutron number)	*Z* (proton number)	Number of nuclei
Even	Even	Even	166
	Odd	Odd	8
Odd	Even	Odd	57
	Odd	Even	53

Nuclei with even numbers of neutrons and even numbers of protons seem to be the most stable. Fig 2.3 gives a plot of the number of neutrons against the number of protons in stable natural nuclei. A study of this plot helps us predict the way a nucleus is likely to disintegrate. Three distinct cases may be identified.

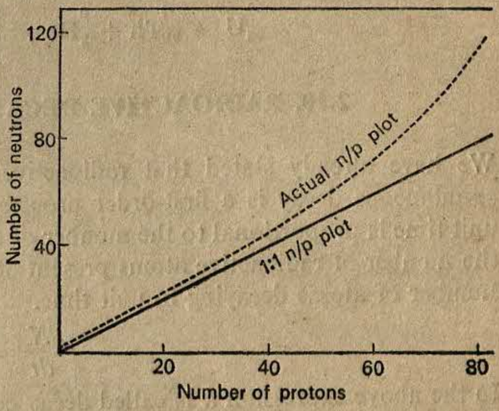


Fig. 2.3. Neutron-proton plot in stable nuclei

1. Neutron/proton ratio too high: If the *N/P* is too high compared to that in a stable isotope i.e. if the nucleus lies above the actual *N/P* in Fig 2.3 then the conclusion is that the nucleus has too many neutrons than is required for stability. Such a nucleus will tend to disintegrate in a way that the number of the neutrons decreases. In other words it will tend to increase the number of the protons. This can be achieved if a neutron breaks down into a proton and an electron. This electron will then be ejected from within the nucleus with a tremendous velocity. So elements with high *N/P* ratio are likely to be beta emitters. Carbon—14 isotope has more neutrons than the stable carbon—12. So carbon—14 is a beta emitter. Cobalt—60 has one neutron in excess of the stable cobalt—59. This, too, is a beta emitter. Given below are some examples.

$$ {}^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}e \ ; \ {}^{133}_{53}\mathrm{I} \rightarrow {}^{133}_{54}\mathrm{Xe} + {}^{0}_{-1}e $$

$$ {}^{60}_{27}\mathrm{Co} \rightarrow {}^{60}_{28}\mathrm{Ni} + {}^{0}_{-1}e \ ; \ {}^{19}_{8}\mathrm{O} \rightarrow {}^{19}_{9}\mathrm{F} + {}^{0}_{-1}e $$

2. Neutron/proton ratio too low : Such a case means that the isotope concerned has too few neutrons than is called for stability. Such elements will tend to increase their number of neutrons at the expense of protons. This is possible only when a proton breaks down into a neutron and a positron (i.e. the positive counterpart of the electron). Nitrogen—13 has less neutron than the stable nitrogen—14. So nitrogen—13 is a positron emitter. Carbon—11 is also deficient in the number of neutrons compared to the stable carbon—12. So carbon—11 decays by emitting positron. Some examples are given below:

$$^{13}_{7}N \rightarrow ^{13}_{6}C + ^{0}_{+1}e \; ; \quad ^{121}_{53}I \rightarrow ^{121}_{52}Te + ^{0}_{+1}e$$

$$^{10}_{6}C \rightarrow ^{10}_{5}B + ^{0}_{+1}e \; ; \quad ^{11}_{6}C \rightarrow ^{11}_{5}B + ^{0}_{+1}e$$

3. **Natural alpha emitters** : These elements usually have their atomic numbers above 82 and mass numbers greater than 200. By the time these elements are found in the periodic table too many protons have been added. Although there are indeed a large number of neutrons, these are not sufficient binding material to negate the severe proton-proton repulsion. As a result these elements mostly decay by alpha emission. Some examples are cited below :

$$^{238}_{92}U \rightarrow ^{234}_{90}Th + ^{4}_{2}He \; ; \quad ^{226}_{88}Ra \rightarrow ^{222}_{86}Rn + ^{4}_{2}He$$

2.10. RADIOACTIVE DECAY RATE CONSTANTS

We have already stated that radioactive disintegration is spontaneous. This spontaneous decay is a first-order process. The number of disintegrations per unit time is proportional to the number of atomic nuclei present. If N represents the number of radioactive atoms present at zero time, then dN/dt represents the number of atoms decaying in unit time.

$$-\frac{dN}{dt} = kN$$

In the above expression k is called decay constant or the disintegration constant. Negative sign indicates that as a result of the decay process there is a decrease in the number of atoms. By rearrangement the following expression can be written :

$$-\frac{dN}{N} = kdt \quad \therefore \; -(dN/N)/dt = k$$

If we put dt equal to unit time then a meaning of the decay constant is immediately clear. *The decay constant is the fraction of the radioactive atoms undergoing decay in unit time.* Integration of the above expression gives the following results. A characteristic index of the radioactivity is obtained when we put $N = \frac{1}{2} N_o$. This means we are stydying the condition when the activity is reduced to half. The time required to achieve this situation is expressed as $t_{\frac{1}{2}}$ called the half-life of the radioelement. The following manipulations give us a relation between half life and the decay constant. The relation tells us that the larger the half life the smaller the decay constant and conversely the smaller the half-life the larger the decay constant.

$$-\int_{No}^{N} \frac{dN}{N} = \int_{o}^{t} kdt \; ; \; -\int_{No}^{N} d\,(\ln N) = \int_{o}^{t} kdt$$

$$\therefore\ -\ln\frac{N}{N_o} = kt\ ;\quad 2.303\ \log\frac{N_o}{N} = kt$$

Putting $N = \frac{1}{2} N_o$ we have $2.303\ \log 2 = kt_{\frac{1}{2}}\ ;\ \therefore t_{\frac{1}{2}} = \dfrac{0.693}{k}$

Compare the following data :

Element	Half-life	Decay constant
Uranium-238	4.5×10^{9} years	1.5×10^{-10} year^{-1}
Radium-226	1590 years	4.3×10^{-4} year^{-1}
Radon-222	3.82 days	2.1×10^{-6} sec^{-1}

Problem 1. A radioisotope deacays at such a rate that one-fourth of the original amount only remains after 68 minutes. Calculate the decay constant and the half life. (given log 4 = 0.6021)

Here N_o is 1 while N is $\frac{1}{4}$th. So that we can write :

$$2.303\ \log\ (N_o/N) = kt\quad ;\quad 2.303\ \log(1/\tfrac{1}{4}) = k\times68\ \text{min.}$$

$$2.303\ \log 4 = k\times68\ \text{min}\quad ;\quad 2.303\times0.6021 = k\times86\ \text{min.}$$

$$k = (2.303\times0.6021)/68\ \text{min} = 0.02\ \text{min}^{-1}$$

$$t_{\frac{1}{2}} = 0.693/k = 0.693/(0.02\ \text{min}^{-1}) = 34.6\ \text{min.}$$

Problem 2. What is the alpha activity in disintegrations per min for a 0.001 gm of radium-226 (half-life = 1590 years)

Activity in terms of disintegration per min means the decay constant in min.

$$t_{\frac{1}{2}} = 0.693/k\ ;\ k = 0.693/t_{\frac{1}{2}} = 0.693/1590\ \text{years}$$

$$= 0.693/(1590\times365\times24\times60\ \text{min})$$

$$= 0.8\times10^{-9}\ \text{min}^{-1}$$

Problem 3. In a cave in France substances have recorded a carbon-14 beta disintegration rate of 2.25 disintegrations per minute per gm of carbon. Calculate how old these substances are given the fact that in living organisms the decay rate is 15.3 disintegrations per gm of carbon per minute. (given log 7 = 0.845; half-life = 5668 years). Here N_o and N are to be taken in terms of initial and the recorded number of disintegrations per gm of carbon per min.

$$2.303\ \log\ (N_o/N) = kt\quad ;\quad \text{But}\ k = 0.693/t_{\frac{1}{2}}$$

$$2.303\ \log\ (15.3/2.25) = (0.693/5668\ \text{year})\ t$$

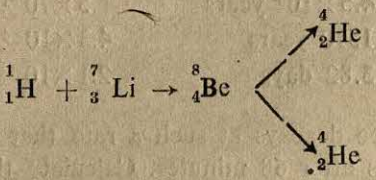
$$t = \frac{2.303\times\log\ 7\times5668\ \text{year}}{0.693} = 15303\ \text{years}$$

2.11. ARTIFICAL TRANSMUTATION AND ARTIFICIAL RADIOACTIVITY

In the year 1919 Rutherford made another startling discovery that artificial transmutation of elements can be achieved when suitable elements are bombarded by fast moving alpha particle. The reaction that was the forerunner of many new things to come was :

$$ {}^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{17}_{8}O + {}^{1}_{1}H \qquad ({}^{1}_{1}H = \text{proton}) $$

Another such artificial reaction is the reaction between lithium and fast moving proton giving rise to an unstable beryllium-8 nucleus which then splits up into two helium nuclei :



$$ {}^{1}_{1}H + {}^{7}_{3}Li \rightarrow {}^{8}_{4}Be \left\langle \begin{matrix} \nearrow {}^{4}_{2}He \\ \searrow {}^{4}_{2}He \end{matrix} \right. $$

The above artificial transmutation is shown pictorially in Fig 2.4

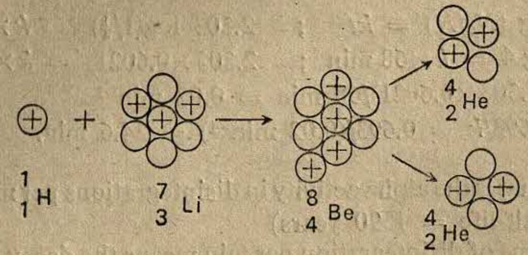


Fig. 2.4. Artificial transmutation of lithium-7 by proton

Another artificial transmutation reaction which we shall always cherish down the memory lane is the one that led to the discovery of the fundamental particle neutron :

$$ {}^{9}_{4}Be + {}^{4}_{2}He \rightarrow {}^{12}_{6}C + {}^{1}_{0}n $$

Studies on artificial transmutation of various types brought to light that these reactions can also produce radioactive elements which do not occur in nature. To Irene Curie, the eldest daughter of the Curies, and her husband Joliot-Curie goes the credit of discovering the first artificially produced radioactive element. They bombarded thin aluminium foil by fast moving alpha particle. This reaction led to the formation of phosphorus-30 and a neutron. But an interesting sapect was that the reaction also started giving off positron. The positron emission continued even when the alpha particle source was withdrawn. This could only mean that the phosphorus-30 produced in the reaction must be radioactive. Our knowledge of the *N*/*P* ratio of phosphorus-30 shows that it has one neutron less than the stable phosphorus-31. Hence it is expected to decay via positron emission giving a stable nucleus of silicon-30.

$$ {}^{27}_{13}Al + {}^{4}_{2}He \rightarrow {}^{30}_{15}P + {}^{1}_{0}n \;;\quad {}^{30}_{15}P \rightarrow {}^{0}_{+1}e + {}^{30}_{14}Si $$

Other accelerated projectiles i.e. bombarding particles have also been successfully used for the purpose :

neutron : ${}^{23}_{11}\mathrm{Na} + {}^{1}_{0}n \rightarrow {}^{23}_{10}\mathrm{Ne} + {}^{1}_{1}\mathrm{H}$ ${}^{23}_{10}\mathrm{Ne} \rightarrow {}^{23}_{11}\mathrm{Na} + {}^{0}_{+1}e$

deuteron : ${}^{32}_{16}\mathrm{S} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{30}_{15}\mathrm{P} + {}^{4}_{2}\mathrm{He}$; ${}^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}e$

2.12. TRANSURANIUM ELEMENTS

In our nature elements of mass numbers greater than 200 are usually radioactive. The last naturally occurring radioactive element is uranium. Elements beyond uranium might have existed long back and by now had decayed to be non-existent. These elements surely had short half-lives. It has been possible to synthesise some trans-uranium elements by artificial transmutation reactions. Some examples are given in Table 2.5.

Table 2.5. Syntheses of Trans-Uranium Elements

Artificial Transmutation	Trans-Uranium Elements
${}^{238}_{92}\mathrm{U} + {}^{2}_{1}\mathrm{H} \longrightarrow$	${}^{238}_{93}\mathrm{Np}$ (Neptunium) $+ 2{}^{1}_{0}n$
${}^{238}_{92}\mathrm{U} + {}^{4}_{2}\mathrm{He} \longrightarrow$	${}^{240}_{94}\mathrm{Pu}$ (Plutonium) $+ 2{}^{1}_{0}n$
${}^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \longrightarrow$	${}^{242}_{95}\mathrm{Am}$ (americium) $+ {}^{1}_{1}\mathrm{H} + {}^{1}_{0}n$
${}^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \longrightarrow$	${}^{240}_{96}\mathrm{Cm}$ (Curium) $+ 3{}^{1}_{0}n$
${}^{244}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \longrightarrow$	${}^{245}_{97}\mathrm{Bk}$ (Berkelium) $+ {}^{1}_{1}\mathrm{H} + 2{}^{1}_{0}n$
${}^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \longrightarrow$	${}^{245}_{98}\mathrm{Cf}$ (Californium) $+ 5{}^{1}_{0}n$
${}^{238}_{92}\mathrm{U} + {}^{14}_{7}\mathrm{N} \longrightarrow$	${}^{247}_{99}\mathrm{Es}$ (Einsteinium) $+ 5{}^{1}_{0}n$
${}^{238}_{92}\mathrm{U} + {}^{16}_{8}\mathrm{O} \longrightarrow$	${}^{250}_{100}\mathrm{Fm}$ (Fermium) $+ 4{}^{1}_{0}n$
${}^{253}_{99}\mathrm{Es} + {}^{4}_{2}\mathrm{He} \longrightarrow$	${}^{256}_{101}\mathrm{Md}$ (Mendeleevium) $+ {}^{1}_{0}n$
${}^{246}_{96}\mathrm{Cm} + {}^{13}_{6}\mathrm{C} \longrightarrow$	${}^{251}_{102}\mathrm{No}$ (Nobelium) $+ 8{}^{1}_{0}n$
${}^{252}_{98}\mathrm{Cf} + {}^{10}_{5}\mathrm{B} \longrightarrow$	${}^{257}_{103}\mathrm{Lw}$ (Lawrencium) $+ 5{}^{1}_{0}n$
${}^{242}_{94}\mathrm{Pu} + {}^{22}_{10}\mathrm{Ne} \longrightarrow$	${}^{260}_{104}\mathrm{Ku}$(Kurchatovium) $+ 4{}^{1}_{0}n$

2.13. SEPARATION AND USES OF ISOTOPES

2.13.1. Separation of isotopes. In section 2 we have given several definitions of isotopes. Isotopes vary only in mass. Their atomic numbers are the same i.e. they also have the same number of the electrons. As a result all isotopes have similar chemical properties. We can thus appreciate that chemical methods will not be suitable for their separation. Instead we have to make use of such methods of separation which are mass dependent. A short resume of some important separation methods is given below:

1. *Gaseous diffusion* : Obviously this method will be applicable to those elements which are themselves gaseous or whose selected compounds are gaseous. The most outstanding example is the gaseous diffusion of hexafluoride of uranium 238 and uranium-235. Graham's law states that the rate of diffusion of gaseous molecules through a porous barrier is inversely proportional to the square root of the molecular weights. Thus a lighter isotopic compound will diffuse at a faster rate than its heavier counterpart. $^{235}UF_6$ and $^{238}UF_6$, in a natural mixture, were allowed to diffuse through hundreds of porous tubes. At one end of this series of operations there was satisfactory enrichment of $^{235}UF_6$ from which pure uranium-235 was isolated. This was later used in the making of the atomic bombs that rocked Hiroshima and Nagasaki. These explosions of unprecedented dimension represented at the same time the triumph and tragedy of uncontrolled nuclear reaction (section 2.16).

2. *Thermal diffusion* : This method depends upon the fact that if a difference in temperature can be maintained inside a tube through which is circulated a gaseous isotopic mixture then the lighter isotope will collect towards the hotter part while the heavier isotope will gather towards the colder part of the tube. In practice a wide-bored tube is heated by suspending an electrically heated platinum wire centrally. The outside wall of the tube is kept cool by circulating water. The temperature of the platinum wire is around 600°C. The lighter isotope moves upwards along the heated wire while the heavier isotope moves down below along the colder wall of the tube. Using many such tubes isotopic gaseous mixtures like nitrogen-14/nitrogen-15, HCl^{35}/HCl^{37} could be successfully separated by leading the mixture through these tubes in succession.

3. *Electrolytic Separation* : This method has been found to be very effective in the separation of the two isotopes of hydrogen of mass numbers 1 and 2, called respectively protium and deuterium. Washburn and Urey noted on continued electrolysis of alkaline water the heavy isotope continues to accumulate in the electrolyte in perference to the lighter isotope. Usually 2 litres of $0.5N$ NaOH is used as electrolyte with nickel electrodes. On prolonged electrolysis the electrolyte gets concentrated in NaOH. As the volume gets reduced to around 200 ml the electrolysis is suspended and the concentrated NaOH solution is treated with CO_2 in order to remove the NaOH as Na_2CO_3. Afterwards the water is again made $0.5N$ in NaOH and electrolysis restarted. The process is continued till the volume is reduced down to around 80 ml. The NaOH is finally removed and the

heavy water D_2O is collected. On electrolysis of this heavy water we get the heavy hydrogen isotope.

4. *Fractional distillation method* : This method has been used with success for separation of the isotopes of mercury. There is a slight difference in the boiling point and vapour pressure of isotopes of a liquid element like mercury. Liquid mercury is allowed to evaporate in an apparatus shown in Fig 2.4. The lighter isotopes preferentially evaporate earlier and condense at the cold surface of the apparatus. The heavier isotope is drawn out through the stop-cock. The lighter isotope is again evaporated to get another lot of lighter mercury. Several repititions of such fractional distillation and condensation give a separation of murcury-199 from mercury-200 and mercury-202.

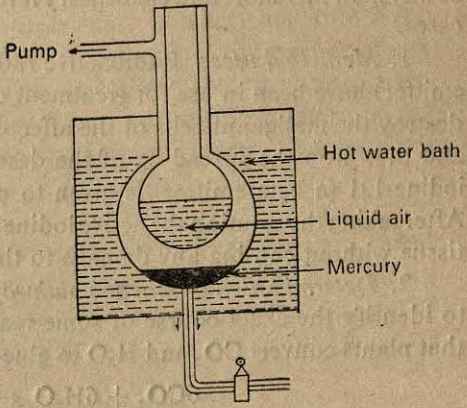


Fig. 2.4. Apparatus for separation of mercury isotopes.

5. *Aston's mass spectrograph method:* Although the principle of the method is quite simple it involves lot of technical perfection for its success. The apparatus has three distinct parts : an arrangement for converting the isotopic species into positively charged ions ; the next part is an evacuated dispersing region where the positive ions are made to travel through an electric field and then through a magnetic field ; and the final part is a detector/collector of the positively charged ions. Since the element is the same and assuming that the positive charge on the isotopic species is also the same, then the trajectories followed by the ions will be decided by their (e/m). Ions having the same (e/m) will follow the same path. Ions whose (e/m) is the largest necessarily have the smallest mass and these species will have the smallest radius of curvature after traversing the electric and magnetic fields. Such an apparatus (Fig 2.5) is first standardised using a single isotopic species like oxygen-16. The detector usually is a photographic plate which records the mass spectrum with respect to the standard oxygen-16. Instead of the detector a collector may be placed at predetermined positions to receive the different isotopic species. This method has worked well for neon-20/neon-22, uranium-235/uranium-238. The positive ions are generated by bombarding the gaseous atoms with a beam of energetic electrons from a heated filament. The method is also called

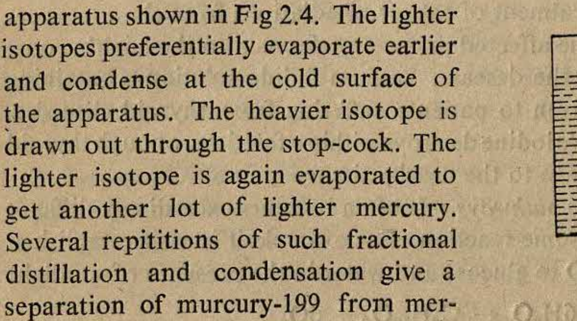


Fig. 2.5. Schematic drawing of Aston's mass spectrograph

electromagnetic method. It is not suitable for large-scale separation but is often valuable for research samples.

2.13.2. Uses of isotopes. Isotopes have come to the service of mankind in a variety of ways. In this short and elementary level book we propose to depict a few selected cases.

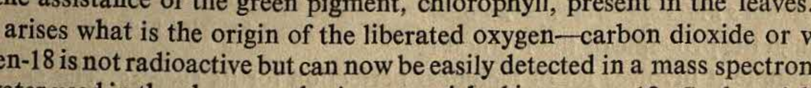
1. *Medicinal uses* : Radioactive radium (an alpha emitter), cobalt-60 (a beta emitter) have been in use for treatment of cancer. Radiations from these sources destroy the malignant cells of the affected parts in preference to the healthy ones and thus stop the spreading of the desease. Sodium iodide solution containing iodine-131 (a beta emitter) is given to patients suffering from thyroid disorder. After taking the solution the active iodine destroys within a few days enough thyroid tissue without causing any damage to the nearby tissue.

2. *Determination of reaction pathways* : It often becomes exceedingly difficult to identify the exact course of some reaction. For example it is well established that plants convert CO_2 and H_2O to glucose and water in the presence of sunlight

$$6CO_2 + 6H_2O \leftarrow C_6H_{12}O_6 + 6O_2$$

with the assistance of the green pigment, chlorophyll, present in the leaves. The point arises what is the origin of the liberated oxygen—carbon dioxide or water. Oxygen-18 is not radioactive but can now be easily detected in a mass spectrometer. The water used in the above synthesis was enriched in oxygen-18. Such enrichment of a particular atom with one of its desired isotopes is called *isotope labelling*. At the conclusion of the experiment it was found that the entire oxygen-18 appeared as the liberated oxygen. So in photosynthesis it is the water oxygen that comes out as free oxygen.

In the following esterification process a natural question arises whether the



$$C_6H_5C\begin{array}{l}{}^{\diagup\!\!\diagup}O\\ {}_{\diagdown}OH\end{array} + CH_3OH \longrightarrow C_6H_5C\begin{array}{l}{}^{\diagup\!\!\diagup}O\\ {}_{\diagdown}O^*CH_3\end{array} + H_2O$$

starred oxygen originates from the alcohol or the acid. Oxygen-18 labelled methyl alcohol was used in the synthesis. It was observed that the ester carried the labelled oxygen and not the liberated water. The oxygen atom in the ester linkage in the above reaction must have come from the alcohol and not the acid. However, the young readers are cautioned that this finding is not universally true for all esterification processes. In some cases the acid oxygen is known to form the ester linkage.

3. *Finding out the age of old relics* : Carbon-14 is a beta emitter while carbon-12 is stable. The atmospheric carbon dioxide maintains an equilibrium of 1 carbon-14 to every 10^{12} carbon-12. All living plants maintain this equilibrium while dead ones cannot. In dead plants the carbon-14 present originally decays by beta emission. With the passage of time the carbon-14 content continues to decrease. By comparing the beta emission with what is found in living bodies it is possible to establish the period or age of the old relic. Living bodies give 15.3 (beta) disintegrations per minute per gm of carbon. By measuring the disintegra-

tions per minute and with the help of the half life of carbon-14 (5668 years) ages of many important relics have been calculated (cf : problem 3 in section 2.10).

2.14. ISOBAR AND ISOTONE

2.14.1. Isobar. Different elements with the same mass numbers are known as isobars. Isobars therefore have different atomic numbers i.e different numbers of protons and different numbers of neutrons. It follows that they must vary widely in their chemical properties. Argo-40 (18 protons and 22 neutrons) and calcium-40 (20 protons and 20 neutrons) are examples of isobars. Another set is : platinum-196 and mercury-196.

2.14.2. Isotone. Different elements with the same number of neutrons are called isotones. Isotones have different atomic numbers and hence possess different chemical properties. Radium-226 (88 protons and 138 neutrons) and actinium-227 (89 protons and 138 neutrons) are examples of isotones.

2.15. NUCLEAR BINDING ENERGY

The total mass of an atom comes from the masses contributed by the protons and the neutrons in the nucleus and the extranuclear electrons. Since the electrons have so very little mass that for our present purpose we shall neglect their contribution. It is always observed that the actual mass of an atom of any element is always less than the mass calculated on the basis of the actual number of protons and neutrons. This difference between the calculated mass and the actual mass is variously called the *mass defect, mass decrement or mass deficiency*. The question is where this missing mass has gone. The answer is : the missing mass i.e. the mass defect has been converted to energy during the formation of the particular atom. This loss of energy has given the real *binding energy* or *stability* to the atom. Einstein had already proposed his famous mass — energy equivalence equation :

$$E = mc^2 \ (m = \text{mass in gm} \ ; \ c = \text{velocity of light})$$

Let us now take the example of the oxygen-16 atom. The atom consists of 8 protons and 8 neutrons in the nucleus and 8 extranuclear electrons. Leaving aside the 8 electrons we have :

mass of 8 protons $= 8 \times 1.00728 = 8.05824$ *amu*
mass of 8 neutrons $= 8 \times 1.00867 = 8.06936$ *amu*

Total mass of 16 nucleons $= 16.12760$ *amu*
Actual mass of oxygen atom $= 15.99491$ *amu*

mass defect $= 0.13269$ *amu*

Putting m equal to 1 gm in the Einstein equation we have :

$$E \text{ (in ergs)} = 1 \times 9 \times 10^{20} \ ; \quad \therefore \ 1 \text{ gm} = 9.00 \times 10^{20} \text{ ergs}$$

Again 1 gm $= 6.02 \times 10^{23}$ *amu* (cf : section 1.5.7.)

1 erg $= 6.24 \times 10^{5}$ *Mev* (*Mev* = million electron volt)

$$\text{Therefore } 1\ amu = \frac{9.00 \times 10^{20} \times 6.24 \times 10^{5}\ Mev}{6.02 \times 10^{23}} = 931\ Mev$$

So the binding energy of oxygen-16 atom

$= 0.13269\ amu = 0.13269 \times 931\ Mev = 123.5\ Mev$

Since oxygen-16 has 16 nucleons binding energy per nucleon

$= 123.5\ Mev/16 = 7.7\ Mev$

Binding energy per nucleon has thus been calculated for all the elements of the periodic table. From a plot of the binding energy per nucleon against mass number the following points emerge :

1. Binding energy increases very fast from hydrogen to lithium, helium and oxygen in the order given.
2. Binding energy is maximum towards mass number 60.
3. Binding energy rapidly begins to fall beyond mass number 200.

It must have gone home by now that the larger the binding energy the stabler the atom is. That the binding energy rapidly falls beyond mass number 200 is a pointer that elements such as radium, uranium do not have stable nuclei. In reality we find that their nuclei undergo radioactive disintegration.

2.16. NUCLEAR FISSION

In section 2.11 we have seen that artificial transmutation reactions (nuclear reactions) by alpha particles, neutrons or deuterons on elements of comparatively low mass numbers lead to the synthesis of elements of close mass numbers. But Hahn and Strassman were amazed to observe that when uranium-235 isotope was bombarded with neutron no element of close mass number could be detected —instead uranium-235 was split into fragments of considerable mass numbers and that more than one such splitting occurred. The fission (splitting) reactions in the case uranium-235 are :

$$\begin{array}{lll} & \nearrow & {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3\,{}^{1}_{0}n + \text{energy} \\ {}^{235}_{92}\mathrm{U} + {}^{1}_{0}n & \longrightarrow & {}^{90}_{37}\mathrm{Rb} + {}^{144}_{55}\mathrm{Cs} + 2\,{}^{1}_{0}n + \text{energy} \\ & \searrow & {}^{87}_{35}\mathrm{Br} + {}^{146}_{57}\mathrm{La} + 3\,{}^{1}_{0}n + \text{energy} \end{array}$$

Interestingly all the above reactions produce neutrons also. These neutrons in turn can bring about fission of further uranium-235 atoms. Such a process may develop into a chain reaction and under optimum conditions may eventually lead to liberation of a huge quantity of energy. We will take up, for example, one of the above three reactions to have an idea about the vastness of the liberated energy.

$${}^{235}_{92}\mathrm{U} + {}^{1}_{0}n \longrightarrow {}^{87}_{35}\mathrm{Br} + {}^{146}_{57}\mathrm{La} + 3\,{}^{1}_{0}n$$

mass of uranium-235	: 234.99340 *amu* ;	Bromin-87	: 86.902800 *amu*
neutron	: 1.00867 *amu* ;	Lanthanum—146	: 145.886500 *amu*
		3 neutrons	3.026010 *amu*
	236.00207 *amu*		235.815131 *amu*

mass defect = 236.00207 *amu* – 235.815131 *amu*
= 0.186760 *amu*

So each uranium-235 atom reveals a mass defect of 0.186760 *amu.* 1 gm of uranium-235 has $(1 \times 6.02 \times 10^{23})/235$ atoms.

Therefore mass defect of 1 gm of uranium-235

$$= (1 \times 6.02 \times 10^{23}) \times 0.186760/235$$

The above mass defect in *amu* may be converted into gm by recalling that 1 gm equals 6.02×10^{23} *amu.* Therefore the mass defect is :

$$= (1 \times 6.02 \times 10^{23} \times 0.186760 \text{ gm})/(235 \times 6.02 \times 10^{23})$$
$$= 0.0008 \text{ gm} = 0.0008 \times 9 \times 10^{20} \times 6.24 \times 10^{5} \ Mev$$
$$= 4.48 \times 10^{23} \ Mev = 0.0008 \times 2.15 \times 10^{10} \text{ K.Cal}$$
$$= 1.7 \times 10^{7} \text{ K.Cal } (1 \text{ gm} = 2.15 \times 10^{10} \text{ K.Cal})$$

Calculations have shown that the reaction becomes self-sustained when about 9000 gm of uranium-235 are used. Huge quantity of energy comes out of the neutron initiated fission reaction of the above quantity of uranium-235. Such uncontrolled fission reaction spelled doom for Hiroshima and Nagasaki.

Scientists have been able to control the above chain reaction by slowing down the neutrons or absorbing many of the neutrons by graphite or cadmium rods or heavy water. Under controlled conditions the nuclear fission of uranium-235 has been utilised abroad and here in our country at Ranapratapsagar, Tarapur and Kalapakkam for generation of electricity.

2.17. NUCLEAR FUSION

In section 2.15 we have seen how the binding energy of nucleons varies with mass number. Fusion of two or more atoms may lead to a species with substantial mass defect. Such mass defect will be given out in the form of energy. Highest mass defect is observed when helium is formed from (1) two deuterons (2) four protons and (3) deuteron and tritium nucleus :

(1) ${}^{2}_{1}\text{H} + {}^{2}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + \text{energy}$

mass defect = $(2 \times 2.04199) - (4.0015) = 0.0269$ *amu* = 25.04 *Mev*

(2) ${}^{1}_{1}\text{H} + {}^{1}_{1}\text{H} + {}^{1}_{1}\text{H} + {}^{1}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + 2\,{}^{0}_{+1}e + \text{energy}$

mass defect = $(4 \times 1{,}00728) - (4.0015) = 0.0276$ *amu* = 25.69 *Mev*

(3) $^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n$ + energy

mass defect $= (2.014199 + 3.016049) - (4.0015 + 1.00867)$ *amu*
$= 0.02008$ *amu* $= 18.69$ *Mev*

Lot of thermal energy will be given out from the above nuclear fusion reactions. The above reactions occur during the explosion of a hydrogen bomb. It is also believed that the ultimate expression of the reactions going on inside the sun is :

$$4\,^{1}_{1}H \longrightarrow ^{4}_{2}He + 2\,^{0}_{+1}e + \text{energy}$$

EXERCISES

1. How would you proceed to establish that radioactivity is a nuclear phoenomenon?

2. What are the particles ejected during natural radioactivity? Describe their properties on a comparative basis.

3. How did Rutherford demonstrate that alpha particles are doubly charged helium ion?

4. Is there any distinction between beta rays and electrons?

5. Explain the group displacement law enunciated by Fajans and Soddy. State how it allows isomeric species to be included in the same group of the periodic table.

6. What is the meaning of half life of a radioactive element? Half lives of uranium-238 and radium-226 are 4.5×10^{9} and 1590 years respectively. What conclusion would you make about the stability of their nuclei?

7. Write balanced equations in the following cases :

(*a*) $^{14}_{6}C$ emits beta ray (*b*) $^{234}_{92}U$ emits an alpha ray

8. The half life of an isotope is 22.6 minutes. Calculate its decay constant.

9. What are the particles likely to be emitted by the following radioactive species?

(*a*) sodium-24 (*b*) oxygen-15 (*c*) iodine-121

10. What is mass defect? How does it fit with nuclear fission and nuclear fusion?

11. Give a concise account of the different methods of separation of isotopes.

12. Write short notes on artificial transmutation and artificial radioactivity.

CHAPTER 3

THE PERIODIC TABLE

3.1. EARLY ATTEMPTS TOWARDS PERIODIC CLASSIFICATION OF ELEMENTS

Periodic classification of elements has been hailed as one of the most outstanding and useful generalisations ever made in the domain of chemistry. Even today whenever we try to look critically at some particular property of an element the periodic classification works in our mind as a backdrop. Since the early attempts to arrive at an acceptable form of classification we have indeed come a long way to the present form of the periodic table. Among the early thinkers were Dobereiner, Lensen, Newlands, Lothar Meyer and Mendeleev. In those days these chemists had very few data related to the chemical elements and their compounds at their disposal. None the less with these limited data they went about their task in right earnest. Lothar Meyer described his atomic volume curve in which he plotted atomic volume of the elements against their atomic weights. Particularly striking was the revelation that in this multi-crest plot the crests were always occupied by the alkali elements. That the alkali metals have similar chemistry was immediately demonstrated. But it did not go a long way to allow us similar generalisations in respect of other known elements. Ultimately it was left to Dimitri Ivanovich Mendeleev to propose his periodic table and make a real beginning in this area. To Mendeleev goes the major credit and he will be remembered for his contribution of far-reaching consequence in chemistry.

3.2. MENDELEEV PROPOSES HIS PERIODIC TABLE

At the time (1869) of Mendeleev only a few properties of the elements and their compounds were known. These were atomic weight, atomic volume, melting point, boiling points of the elements, and some compound of the elements and their properties. Mendeleev's thinking was somewhat like this : An element has a characteristic atomic weight and has a characteristic set of properties. Different elements have different atomic weights and different chemical properties. Again atoms are the smallest building blocks of elements. He therefore firmly believed that there must be a connection between atomic weights and chemical properties. In order to check how far his thinking was valid he wrote down, so to say, 'confidential character roles' of the elements (about sixty) discovered at his time. Careful scrutiny of these character rolls revealed that elements with comparable chemical properties appeared at certain intervals. He then proposed his famous Periodic Law :

Properties of chemical elements are periodic functions of their atomic weights.

Based on the above law Mendeleev developed his periodic table of 1871

(Table 3.1) based on atomic weights. Some salient points of his periodic table are given below :

1. If the elements are arranged in order of atomic weights a repitition of chemical properties are observed at certain intervals.

2. The elements could be arranged into several horizontal rows called *periods* and some vertical columns called *groups*. Valence of an element can very well be guessed from its position in the table. Elements belonging to the same group possess the same valence and hence similar properties. Elements of different groups have different properties.

3. Those elements with very similar properties such as iron, cobalt, nickel or osmium, iridium and platinum have very close atomic weights.

4. Elements which appear abundantly in the earth's crust usually have low atomic weights and differ widely in their chemical properties. These elements were termed *typical elements*.

5. Any discrepancy in the atomic weight of any element may be guessed from an examination of the atomic weights of the neighbouring elements.

So confident Mendeleev was about his periodic law that he left some gaps in his periodic table indicating that the elements corresponding to these gaps had not yet been discovered. Gallium, scandium and germanium were among the elements for which he had left gaps in his table. These indeed were discovered at later dates and it does enormous credit to the originator of the periodic table that the predicted properties corroborated very well with the actual properties found. Given below is the example of the element coming below silicon in group IV. This was named by Mendeleev *eka-silicon* which was later discovered and named germanium.

Property	Predicted for eks-silicon	Found for germanium
Atomic Weight	72	72.60
Density	5.5	5.36
Formula of oxide	MO_2	GeO_2
Density of oxide	4.7	4.703
Formula of chloride	MCl_4	$GeCl_4$
Density of chloride	1.9	1.887
Boiling point of chloride	below 100°C	86°C
Formula of ethyl compound	$M(C_2H_5)_4$	$Ge(C_2H_5)_4$
Boiling point of ethyl compound	160°C	160°C
Density of the ethyl compound	0.96	close to 1

3.3. A SCRUTINY OF MENDELEEV'S PERIODIC TABLE

The 1871 version of Mendeleev's table is depicted in Table 3.1. At the time he proposed his table the noble gases and the lanthanides remained undiscovered. So there had to be some shortfall in his table. None the less his major point that

Table 3.1. Mendeleev's Periodic Table based on 1871 Atomic Weights

Period → Group ↓	I R_2O	II RO	III R_2O_3	IV RH_4 RO_2	V RH_3 R_2O_3	VI RH_2 RO_3	VII RH R_2O_7	VIII RO_4
1	H = 1			C = 12	N = 14	O = 16	F = 19	
	Li = 7	Be = 9.4	B = 11					
2	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
3	K = 39	Ca = 40	* = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56
	Cu = 63	Zn = 65	* = 68	* = 72	As = 75	Sc = 78	Br = 80	Ni = 59
								Co = 59
4	Rb = 85	Sr = 87	Y = 88	Zr = 90	Nb = 94	MO = 96	* = 100	Ru = 104
	Ag=108	Cd = 112	In = 113	Sn = 118	Sb=122	Te=125	I = 127	Rh = 104
								Pd = 106
5	Cs = 133	Ba = 137	Di = 138	Ce = 140				
	Au=199	Hg=200	Er = 178	La = 180	Ta = 182	W = 184		Os = 195
			Tl = 204	Pb=207	Bi=208			Ir = 197
				Th = 231		U = 240		Pt = 198

* indicates predicted elements

propertes of elements are periodic functions of atomic weights is very well borne out by facts. Let us take the two short periods :

I	II	III	IV	V	VI	VII
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

Lithium and sodium are both alkali elements. They possess the same valence, namely + 1, and form similar fluoride, chloride, bromide, etc. These halides have comparable properties. These are basically ionic compounds, dissolve in water to ionise into metal cations, Li^+ and Na^+ and halide anions, X^-. These are all high melting solids. Both lithium and sodium react with hydrogen to form LiH and NaH. Both these hydrides are again ionic in nature and in fused state ionise as the corresponding metal cation and the hydride anion H^-. On electrolysis in both cases hydrogen is liberated at the anode :

$LiH \rightarrow Li^+ + H^-$; at the cathode : $Li^+ + e \rightarrow Li$
at the anode : $H^- \rightarrow H + e$; $2H \rightarrow H_2$
$NaH \rightarrow Na^+ + H^-$; at the cathode : $Na^+ + e \rightarrow Na$
at the anode : $H^- \rightarrow H + e$; $2H \rightarrow H_2$

We thus see, according to Mendeleev's assertion, that properties repeat after certain interval of atomic weight : from an atomic weight of 7 in lithium to 23 in sodium. If we compare fluorine and chlorine we find that both form diatomic molecules, are strong oxidants, their fused alkali salts are ionised to produce mononegative anions (F^-, Cl^-). On electrolysis the halogens are liberated at the anodes. Thus on the whole Mendeleev did produce some revolutionary generalisation at his time.

Mendeleev arranged all the known elements into *five horizontal rows called periods* and *eight vertical columns called groups. This arrangement of elements into periods and groups is known as the periodic table.* Mendeleev's original table had two short periods each containing seven elements (excepting hydrogen), two long periods each containing 17 elements (including those undiscovered) and the last period remaining rather incomplete with 18 elements. Mendeleev had to subdivide his groups into two i.e. A and B because of some differences of properties found in members placed in the same group. For example potassium and copper were placed in group IA and IB respectively. We know that both these elements have the same valence + 1, although copper has + 2 as well. The differences were large enough to warn Mendeleev that he could not place copper directly below potassium in the same group. Thus group IA had Li, Na, K, Rb and Cs while group IB had Cu, Ag and Au.

3.4. MENDELEEV'S 1871 TABLE UNDERGOES REVISION IN THE LIGHT OF MODERN ELECTRONIC STRUCTURE

We recall from Chapter 1 that an atom has two distinct parts : the nucleus and the extranuclear electrons. The nucleus contains the vital protons and the neutrons.

For electroneutrality the number of extranuclear electrons is the same as the protons. The protons vary from member to member. Moseley showed that the X-ray spectra of different elements are characteristic of the serial order they occupy in the periodic table. A plot of the square root of the highest frequency (expressed as wave number) of the X-ray spectra against atomic weights gave a straight line with a few points off the line. Instead, when this plot was made against the serial orders of the elements in the table a perfect straight line was obtained without any stray point. This serial number, called atomic number, was considered more fundamental than atomic weight. Atomic number was correlated to the nuclear charge of the atom. Atomic number, being the nuclear charge, increased by one unit from one element to the next in the periodic table. Thus Mendeleev's periodic law was modified to the following form :

Properties of chemical elements are periodic functions of their atomic numbers.

Based on the above periodic law Mendeleev's original 1871 table has been changed to the modern version given in Table 3.2. This table contains many more elements than the 1871 table because a lot more of elements were discovered after Mendeleev. In the modern light of electronic structure and in view of the elements discovered at a later date the following defects of Mendeleev's table are apparent :

1. Elements have to be arranged in order of increasing atomic number. Based on atomic weight Mendeleev placed tellurium (atomic weight 125) in group VI and iodine (atomic weight 127) in group VII. Later precise determinations revealed that the atomic number and atomic weights of the elements are : Te, 52, 127.6 ; I, 53 ; 126.9. On the basis of rather inaccurate atomic weight Mendeleev placed tellurium before iodine. But the precise atomic weight data would now indicate, according to Mendeleev, a reversal of positions i.e. tellurium in group VII and iodine in group VI. But we are saved from this property-wise inconsistent positions as a result of the discovery that atomic number is more fundamental than atomic weight. Thus tellurium and iodine are there in the groups shown in Mendeleev's table of 1871 not on the basis of atomic weight but on the basis of atomic number. Correct positions of the pairs : argon/potassium, cobalt/nickel have also been fixed on the merit of the atomic numbers of the elements.

2. All the noble gases, helium, neon, argon, krypton, xenon and radon were discovered after Mendeleev. All these elements are extremely inert in their chemical activity. Hence a separate new group, called O (zero) group, has been introduced in the periodic table after group VIII.

3. At the time of Mendeleev lanthanum and the following 14 elements, together called *lanthanides*, were not all discovered. The atomic weights of a few of them known at his time were wrong. Now we know that lanthanum and the next 14 elements from cerium to lutecium (Chapter 1.8) have very similar properties although their atomic numbers and atomic weights are increasing gradually. Since with increasing atomic number electrons are being added to a $4f$ shell which is shielded by $5s^2$ and $5p^6$ electrons (in their trivalent cations) their chemistries

Table 3.2. Revised Mendeleev Table based on Atomic Number

Period →	I		II		III		IV		V		VI		VII		VIII	O
↓ Group	A	B	A	B	A	B	A	B	A	B	A	B	A	B		
1	${}_{1}$H															${}_{2}$He
2	${}_{3}$Li		${}_{4}$Be			${}_{5}$B		${}_{6}$C		${}_{7}$N		${}_{8}$O		${}_{9}$F		${}_{10}$Ne
3	${}_{11}$Na		${}_{12}$Mg			${}_{13}$Al		${}_{14}$Si		${}_{15}$P		${}_{16}$S		${}_{17}$Cl		${}_{18}$Ar
4	${}_{19}$K		${}_{20}$Ca		${}_{21}$Sc		${}_{22}$Ti		${}_{23}$V		${}_{24}$Cr		${}_{25}$Mn		${}_{26}$Fe, ${}_{27}$Co, ${}_{28}$Ni	${}_{36}$Kr
		${}_{29}$Cu		${}_{30}$Zn		${}_{31}$Ga		${}_{32}$Ge		${}_{33}$As		${}_{34}$Se		${}_{35}$Br		
5	${}_{37}$Rb		${}_{38}$Sr		${}_{39}$Y		${}_{40}$Zr		${}_{41}$Nb		${}_{42}$Mo		${}_{43}$Tc		${}_{44}$Ru, ${}_{45}$Rh, ${}_{46}$Pd	${}_{54}$Xe
		${}_{47}$Ag		${}_{48}$Cd		${}_{49}$In		${}_{50}$Sn		${}_{51}$Sb		${}_{52}$Te		${}_{53}$I		
6	${}_{55}$Cs		${}_{56}$Ba		${}_{57-79}$La*		${}_{72}$Hf		${}_{73}$Ta		${}_{74}$W		${}_{75}$Re		${}_{76}$Os, ${}_{77}$Ir, ${}_{78}$Pt	
		${}_{79}$Au		${}_{80}$Hg		${}_{81}$Tl		${}_{82}$Pb		${}_{83}$Bi		${}_{84}$Po		${}_{85}$At		${}_{86}$Rn
7	${}_{87}$Fr		${}_{88}$Ra		${}_{89-104}$Ac**											

*Lanthanides :	${}_{58}$Ce, ${}_{59}$Pr, ${}_{60}$Nd ${}_{61}$Pm, ${}_{62}$Sm, ${}_{63}$Eu, ${}_{64}$Gd, ${}_{65}$Tb, ${}_{66}$Dy, ${}_{67}$Ho, ${}_{68}$Er, ${}_{69}$Tm, ${}_{70}$Yb, ${}_{71}$Lu
** Actinides :	${}_{90}$Th, ${}_{91}$Pa, ${}_{92}$U, ${}_{93}$Np, ${}_{94}$Pu, ${}_{95}$Am, ${}_{96}$Cm, ${}_{97}$Bk, ${}_{98}$Cf, ${}_{99}$Es, ${}_{100}$Fm, ${}_{101}$Md, ${}_{102}$No, ${}_{103}$Lw

remain almost similar. Hence they are rightly given a single place in group IIIA (Table 3.2).

4. Sometimes the variations in the properties of the subgroup A and B elements are wide enough. Making rooms for the two subgroups in the same column is rather undesirable.

5. Mendeleev had placed hydrogen in group I. Although many of its properties are consistent with its position in group I there are some properties akin to the halogens. These properties again were not known at Mendeleev's time eg. its behaviour in LiH, NaH. These properties would also prompt us to allot dual places to hydrogen in groups IA and VIIB.

Despite some deficiencies it has to be admitted that Mendeleev had done a remarkable job—something much ahead of his time.

3.5. THE PRESENT VERSION : THE LONG FORM PERIODIC TABLE

The defects of the modern version of the Mendeleev Table have now been removed by changing over to the universally accepted long form (Table 3.3). The improvements are :

1. The subgroups A and B have been widely separated. Group VIII, which has no subgroups, has been placed in the middle. On the left of group VIII are subgroups IA to VIIA while on the right are the subgroups IB to VIIB and the 0 group.

2. One can easily recognise the representative and the transition elements. Representative elements are presented in groups IA, IIA, IIIB to VIIB and O. Representative elements have earlier been defined (Chapter 1.7) as those which have either filled or totally empty *d* or *f* sublevels. Some people also define representative elements as *s* or *p* block elements. The inherent implication is that these elements have either no *d* or *f* electrons or that these sublevels are completely filled. The region in between groups IIA and IIB is occupied by the transition elements. Transition elements have already been defined as those elements having incomplete *d* or *f* sublevels in their atomic state or in any oxidation state.

3. Position of hydrogen has also been settled by putting this element at the top of both the groups IA and VIIB.

Note that there are a total of 18 vertical columns in the long-form of the periodic table.

3.6. ELECTRON DISTRIBUTION AND POSITIONS OF THE ELEMENTS IN THE PERIODIC TABLE

It is interesting to note that the position of the representative elements in the different periodic groups is in conformity with their electron distribution. The total number of electrons in the outermost quantum shell of a representative element is the group number to which the element belongs. Thus all the alkali elements

Table 3.3 Long form Periodic Table

Period → ↓ Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	O
I	H																H	He
→	1																1	2
II	Li	Be											B	C	N	O	F	Ne
→	3	4											5	6	7	8	9	10
III	Na	Mg											Al	Si	P	S	Cl	Ar
→	11	12											13	14	15	16	17	18
IV	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
→	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
V	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
→	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
VI	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
→	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
VII	Fr	Ra	Ac**															
→	87	88	89															

* Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	58	59	60	61	62	63	64	65	66	67	68	69	70	71
** Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
	90	91	92	93	94	95	96	97	98	99	100	101	102	103

have one electron in their outermost quantum shell and hence they rightly belong to group IA. The alkaline earths have two electrons and therefore they belong to group IIA. Carbon, silicon, etc. have a total of four electrons (s^2p^2) in their outermost quantum shell and so they go to group IVB. Thus we see that periodic classification has an inherent connection with our modern ideas of electronic structure of atoms. Mendeleev was not fortunate to know all these modern developments—yet he did something that does show a distinct link with modern ideas. One more amazing point is that in none of the periods the total number of elements exceeds that permitted by the electron accommodation capacity of the different principal quantum numbers. (The electron distribution of all the elements is given in Table 3.4).

3.7. THE PERIODIC TABLE AND THE POSITIONS OF METALS, NON-METALS AND METALLOIDS

Metals are good conductors of electricity. They usually give cations and form ionic compounds. Non-metals have very poor ability to conduct electricity. Usually in non-metals small discrete molecular units are found. Metalloids (also called semimetals) show low electrical conductivity — much lower than that shown by the metals. Non-metals have even smaller conductivities.

Metallic elements appear in the left-hand portion of the periodic table. Metallic behaviour is observed in the members of groups IA, IIA, the transition elements and the heavier elements of groups IIIB, IVB and VB. On the other hand distinctly non-metallic elements occur at upper right-hand portion of the periodic table. These include the lighter members of groups IVB, VB, VIB and VIIB. The metalloids or the semimetals occur along a diagonal band from boron to tellurium (B, Si, Ge, As, Sb and Te). They separate the metallic elements from the non-metals. These general statements have been made with respect to the long form periodic table (Table 3.3).

Table 3.4. Electron Distribution of Elements

Atomic Number	Element	Symbol	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	6f	6g	6h	7s
1	Hydrogen	H	1																					
2	Helium	He	2																					
3	Lithium	Li	2	1																				
4	Beryllium	Be	2	2																				
5	Boron	B	2	2	1																			
6	Carbon	C	2	2	2																			
7	Nitrogen	N	2	2	3																			
8	Oxygen	O	2	2	4																			
9	Fluorine	F	2	2	5																			
10	Neon	Ne	2	2	6																			
11	Sodium	Na	2	2	6	1																		
12	Magnesium	Mg	2	2	6	2																		
13	Aluminium	Al	2	2	6	2	1																	
14	Silicon	Si	2	2	6	2	2																	
15	Phosphorus	P	2	2	6	2	3																	
16	Sulphur	S	2	2	6	2	4																	
17	Chlorine	Cl	2	2	6	2	5																	
18	Argon	Ar	2	2	6	2	6																	
19	Potassium	K	2	2	6	2	6	—	1															
20	Calcium	Ca	2	2	6	2	6	—	2															
21	Scandium	Sc	2	2	6	2	6	1	2															

Table 3.4. (Continued)

Atomic Number	Element	Symbol	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	5*g*	6*s*	6*p*	6*d*	6*f*	6*g*	6*h*	7*s*
22	Titanium	Ti	2	2	6	2	6	2	2															
23	Vanadium	V	2	2	6	2	6	3	2															
24	Chromium	Cr	2	2	6	2	6	5	1															
25	Manganese	Mn	2	2	6	2	6	5	2															
26	Iron	Fe	2	2	6	2	6	6	2															
27	Cobalt	Co	2	2	6	2	6	7	2															
28	Nickel	Ni	2	2	6	2	6	8	2															
29	Copper	Cu	2	2	6	2	6	9	2															
30	Zinc	Zn	2	2	6	2	6	10	2															
31	Gallium	Ga	2	2	6	2	6	10	2	1														
32	Germanium	Ge	2	2	6	2	6	10	2	2														
33	Arsenic	As	2	2	6	2	6	10	2	3														
34	Selenium	Se	2	2	6	2	6	10	2	4														
35	Bromine	Br	2	2	6	2	6	10	2	5														
36	Krypton	Kr	2	2	6	2	6	10	2	6														
37	Rubidium	Rb	2	2	6	2	6	10	2	6	—	—	1											
38	Strontium	Sr	2	2	6	2	6	10	2	6	—	—	2											
39	Yttrium	Y	2	2	6	2	6	10	2	6	1	—	2											
40	Zirconium	Zr	2	2	6	2	6	10	2	6	2	—	2											
41	Niobium	Nb	2	2	6	2	6	10	2	6	4	—	1											
42	Molybdenum	Mo	2	2	6	2	6	10	2	6	5	—	1											

Table 3.4. (Continued)

Atomic Number	Element	Symbol	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	5*g*	6*s*	6*p*	6*d*	6*f*	[6*g*	6*h*	7*s*
43	Technetium	Tc	2	2	6	2	6	10	2	6	6	—	1											
44	Ruthenium	Ru	2	2	6	2	6	10	2	6	7	—	1											
45	Rhodium	Rh	2	2	6	2	6	10	2	6	8	—	1											
46	Palladium	Pd	2	2	6	2	6	10	2	6	10	—	—											
47	Silver	Ag	2	2	6	2	6	10	2	6	10	—	1											
48	Cadmium	Cd	2	2	6	2	6	10	2	6	10	—	2											
49	Indium	In	2	2	6	2	6	10	2	6	10	—	2	1										
50	Tin	Sn	2	2	6	2	6	10	2	6	10	—	2	2										
51	Antimony	Sb	2	2	6	2	6	10	2	6	10	—	2	3										
52	Tellurium	Te	2	2	6	2	6	10	2	6	10	—	2	4										
53	Iodine	I	2	2	6	2	6	10	2	6	10	—	2	5										
54	Xenon	Xe	2	2	6	2	6	10	2	6	10	—	2	6										
55	Caesium	Cs	2	2	6	2	6	10	2	6	10	—	2	6	—	—	—	1						
56	Barium	Ba	2	2	6	2	6	10	2	6	10	—	2	6	—	—	—	2						
57	Lanthanum	La	2	2	6	2	6	10	2	6	10	—	2	6	1	—	—	2						
58	Cerium	Ce	2	2	6	2	6	10	2	6	10	2	2	6	—	—	—	2						
59	Praseodymium	Pr	2	2	6	2	6	10	2	6	10	3	2	6	—	—	—	2						
60	Neodymium	Nd	2	2	6	2	6	10	2	6	10	4	2	6	—	—	—	2						
61	Promethium	Pm	2	2	6	2	6	10	2	6	10	5	2	6	—	—	—	2						
62	Samarium	Sm	2	2	6	2	6	10	2	6	10	6	2	6	—	—	—	2						
63	Europium	Eu	2	2	6	2	6	10	2	6	10	7	2	6	—	—	—	2						

Table 3.4. (Continued)

Atomic Number	Element	Symbol	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	5*g*	6*s*	6*p*	6*d*	6*f*	6*g*	6*h*	7*s*
64	Gadolinium	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1	—	—	2						
65	Terbium	Tb	2	2	6	2	6	10	2	6	10	9	2	6	—	—	—	2						
66	Dysprosium	Dy	2	2	6	2	6	10	2	6	10	10	2	6	—	—	—	2						
67	Holmium	Ho	2	2	6	2	6	10	2	6	10	11	2	6	—	—	—	2						
68	Erbium	Er	2	2	6	2	6	10	2	6	10	12	2	6	—	—	—	2						
69	Thullium	Tm	2	2	6	2	6	10	2	6	10	13	2	6	—	—	—	2						
70	Ytterbium	Yb	2	2	6	2	6	10	2	6	10	14	2	6	—	—	—	2						
71	Lutecium	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1	—	—	2						
72	Hafnium	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2	—	—	2						
73	Tantalum	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3	—	—	2						
74	Tungsten	W	2	2	6	2	6	10	2	6	10	14	2	6	4	—	—	2						
75	Rhenium	Re	2	2	6	2	6	10	2	6	10	14	2	6	5	—	—	2						
76	Osmium	Os	2	2	6	2	6	10	2	6	10	14	2	6	6	—	—	2						
77	Iridium	Ir	2	2	6	2	6	10	2	6	10	14	2	6	7	—	—	2						
78	Platinum	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9	—	—	1						
79	Gold	Au	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	1						
80	Mercury	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2						
81	Thallium	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	1					
82	Lead	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	2					
83	Bismuth	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	3					
84	Polonium	Po	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	4					

Table 3.4. (Continued)

Atomic Number	Element	Symbol	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	5*g*	6*s*	6*p*	6*d*	6*f*	6*g*	6*h*	7*s*
85	Astatine	At	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	5					
86	Radon	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	6					
87	Francium	Fr	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	6	—	—	—	—	1
88	Radium	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	6	—	—	—	—	2
89	Actinium	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	6	1	—	—	—	2
90	Thorium	Th	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	6	2	—	—	—	2
91	Protactinium	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	—	2	6	1	—	—	—	2
92	Uranium	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	—	2	6	1	—	—	—	2
93	Neptunium	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	5	—	2	6	—	—	—	—	2
94	Plutonium	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	6	—	2	6	—	—	—	—	2
95	Americium	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	7	—	2	6	—	—	—	—	2
96	Curium	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	—	2	6	1	—	—	—	2
97	Berkelium	Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	—	2	6	1	—	—	—	2
98	Californium	Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	—	2	6	—	—	—	—	2
99	Einsteinium	Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	—	2	6	—	—	—	—	2
100	Fermium	Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	—	2	6	—	—	—	—	2
101	Mendeleevium	Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	—	2	6	—	—	—	—	2
102	Nobelium	No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	—	2	6	—	—	—	—	2
103	Lawrencium	Lw	2	2	6	2	6	10	2	6	10	14	2	6	10	14	—	2	6	1	—	—	—	2

EXERCISES

1. The periodic table has been hailed as the greatest generalisation in chemical science. Justify the statement.

2. What was the basis on which Mendeleev had proposed his periodic table? What were the most important of the utilities and the defects of this table?

3. How was this realised that atomic number was a more fundamental property of elements rather than atomic weight? How did it refine Mendeleev's table based on atomic weights?

4. Where in the periodic table would you place the following :

chlorine-35, chlorine-37 ; hydrogen-1, hydrogen-2 ; carbon-12, carbon-14

5. Hydrogen is placed either at the head of the alkalies or at the head of the halogens. Is there any conflict in this dual placement?

6. Compare the original periodic table based on atomic number with the currently accepted long-form.

7. What are the differences between representative and transition elements? Which of these two classes of elements does obey the periodic law better?

8. In which groups of the periodic table the elements with the given electron distributions will be placed? Name the elements.

$1s^2\ 2s^2$; $1s^2\ 2s^2\ 2p^6$; $1s^2\ 2s^2\ 2p^5$; $1s^2\ 2s^2 2p^6\ 3s^2$

9. Discuss how Mendeleev sensed that there are several undiscovered elements. Mention at least one example of such later discovery.

10. Mention some of the properties of elements which vary periodically with atomic number.

CHAPTER 4

PERIODIC PROPERTIES OF ELEMENTS AND COMPOUNDS

4.1. INTRODUCTORY COMMENTS

In the preceding chapter we noted that properties of chemical elements and their compounds were found to be periodic functions of atomic number. Earlier Mendeleev proposed atomic weights to be the deciding factor. The properties, in which Mendeleev sought to find out periodic variations were density, atomic volume, melting and boiling points, valence, chemical formula and properties of compounds. Since the days of Mendeleev there has been a considerable growth of science in general and chemistry in particular. Today we do not go to seek periodicity of properties in any of the items of the Mendeleev era. Most of the chemical and physical properties of the elements follow directly from the electron configurations. The properties which are readily interpreted on the basis of electron configuration and which nicely demonstrate the principle of periodicity are ionisation potential (energy), electron affinity, electronegativity, ionic and covalent radii, etc. Since none of these properties of elements or compounds was introduced earlier we deferred any discussion of the periodic variation of the properties of the elements while moving along (a) a group and (b) a period. It is also pertinent to mention here that a clear conception of these fundamental properties is essential in order to make any worthwhile comparative assessment of the elements belonging to a particular group. These properties will go a long way to help us understand the descriptive chemistry of the elements.

4.2. IONISATION POTENTIAL

This gives us an idea of the binding energies of the electrons in an atom. *Ionisation potential (energy) is defined as the minimum energy required to remove an electron of a gaseous atom to infinity.* The potential required to remove the first electron is called the first ionisation potential. We can thus have a second, third ionisation potentials etc.

atom + first ionisation potential → monopositive cation + electron
monopositive cation + second ionisation potential
→ dipositive cation + electron

Ionisation potential is generally expressed in *electron-volts* (*ev*) (1 *ev* = 1.60 $\times 10^{-12}$ ergs = 23.05 K Cal/mole).

There are several factors which decide the magnitude of the ionisation potential. In order to refresh the memory of the young readers we recall from section 1.6.3 that the energy of an electron moving in an orbit of radius *r* about a nuclear charge $+Ze$ is given by $-\frac{1}{2}Ze^2/r$. This quantity is a measure of the binding energy of the electron. This relation tells us that r remaining fixed the electron will be more and more strongly bound with increasing nuclear charge. Again nuclear charge remaining constant the electron will be more loosely held with increasing distance r. In a multielectron atom the nuclear charge is partly screened from the outermost electrons by the inner electrons of lower energy orbitals. Remembering these realities the following generalisations about the variation of the ionisation potential along a group and a period of the periodic table can be made.

1. As the distance between the outer electrons and the positive nucleus increases the electrons are loosely held. Also the inner electrons shield the outer electrons from the nucleus due to screening effect. The outer electrons do not feel the entire positive charge $+Ze$ but an effective nuclear charge $+Z_{effective}$, which is always less than $+Ze$. Therefore it is only expected that as we go down a group the ionisation potentials will gradually decrease. Note with increasing atomic number in a group electrons are added to new quantum shells which add to the size of the atom :

Group IA	Li	Na	K	Rb	Cs
First I.P. (*ev*)	5.39	5.14	4.34	4.18	3.89

Decreasing ionisation potential indicates greater reactivity.

2. As we move along a period of representative (i.e. *s* and *p* block) elements with increasing atomic number electrons are being added to the same principal quantum number. As a consequence there is no scope of increase in size of the atom, instead there is a slow contraction. Because of this the outer electrons are more tightly held and evidently more energy has to be expended in order to dislodge an electron from its orbital. So along a period of the periodic table the ionisation potential increases with increasing atomic number :

Period II :	Li	Be	B	C	N	O	F
First I.P. (*ev*) :	5.32	9.32	8.29	11.25	14.53	13.61	17.42

The reversal of the order at nitrogen/oxygen has been explained as being due to repulsion between two electrons in the same *p* orbital in oxygen.

3. Ionisation potential increases as more and more electrons are withdrawn. It is quite understandable that compard to a neutral atom withdrawal of an electron from a monopositive cation will require more energy as the electron has to be pulled out against the positive attractive force of the cation. Thus the second I.P is always greater than the first I.P and the third I.P is always greater than the second and so on :

Atom/Ion	Mg	Mg^+	Mg^{2+}
I.P (*ev*)	7.64	15.03	80.12
Atom/Ion	K	K^+	K^{2+}
I.P (*ev*)	4.34	31.81	46.0

Some interesting features are observed when first ionisation potentials are plotted against the atomic numbers of the corresponding elements. There is a periodicity in the values of the first I.P. The plot shows several maxima and minima. Beginning with one of the alkali metals (say, lithium), there is a general trend for the I.P to increase until a maximum is reached at the next noble gas (eg. Ne). This trend is repeated as we move along each period of the periodic table. Thus the inevitable conclusion is : In the periodic table the alkali metals are the most prone to lose their electrons while the noble gases possess the stablest electron configuration. In other words the alkalies are the most reactive while the noble gases are least so.

4.3. ELECTRON AFFINITY

Electron affinity is just opposite to the ionisation potential. *Electron affinity may be defined as the energy released when an atom or ion acquires an electron.* It is a measure of the tendency to acquire an electron. Evidently its magnitude should be equal to the corresponding ionisation potential although sign should be opposite. Unfortuanately electron affinity is also expressed with a positive sign. The first ionisation potential of the lithium atom is 5.39 *ev*. It follows that the monopositive lithium ion would release the same 5.39 *ev* of energy in getting back to the neutral lithium atom i.e. the magnitude of the electron affinity of Li^+ is the same as the I.P. of Li atom.

Since electron affinities of many elements are not known it is not possible to make many generalisations. However it is observed that the electron affinities of the nonmetals are usually larger than those of the metals. In particular the electron affinities of the halogens are very large.

1. Since the halogens are closest to the noble gases they acquire electron most readily. However this trend slowly decreases as we move down from chlorine to iodine :

Atom	F	Cl	Br	I
Electron affinity (*ev*)	3.45	3.61	3.36	3.06

2. Metals have low ionisation potentials. So their desire to acquire electrons has to be low. Thus with the alkalies electron affinity falls with increasing atomic number :

Atom	Na	K
Electron affinity (*ev*)	0.74	0.70

4.4. ELECTRONEGATIVITY

Electronegativity of an element is referred to as the power of dragging electron onto itself from other elements present in a compound. Electron affinity represents the electron dragging power of an isolated gaseous atom while electronegativity is a measure of similar property of an element in combination with other elements in a compound. There is no straightforward way to have a measure of this property. One cannot go far in any discussion of electronegativity without mentioning the name of Linus Pauling. Pauling introduced a scale of electronegativity based on the difference in the bond energies of diatomic elements. Bond energy may be defined as the energy required to be supplied in order to take the two atoms forming the bond to infinity. Pauling noted that the bond energy of a diatomic molecule A—B is always greater than the geometric mean of the bond energies of the homodiatomic molecules A—A and B—B. This difference is larger the larger the deviation of the bond A—B from non-polarity. This means that larger electronegativity difference between two elements would indicate that the bond between them has considerable ionic character. The electron dragging power of chlorine being substantially greater than hydrogen, the chlorine end of the molecule HCl will be more negative than the hydrogen end. We say the molecule HCl has developed polarity which we express as $H^{\delta+}—Cl^{\delta-}$.

According to Pauling, we have the following relation :

$$\triangle = (X_A - X_B)^2 \; ; \; D_{A-B} - (D_{A-A} \cdot D_{B-B})^{\frac{1}{2}} = \triangle$$

where X_A and X_B are the electronegativities. Usually bond energies are available in K Cal/mole. In order to express the difference in the bond energies in electron-volts it is divided by 23.05 (1 *ev* = 23.05 K Cal/mole)

$$\text{Thus } X_A - X_B = \sqrt{\triangle/23.06}$$

The energy difference thus expressed usually stays in the range 0.7 to 4. Since this is a difference Pauling arbitrarily assigned to fluorine the figure 4, this element being the most electronegative in the entire periodic table. At this point we would like to mention that although the electronegativity difference of two elements appears to be expressed in *ev*, electronegativity itself is to be considered as a number since there is not much sense in saying that when a fluorine containing bond is formed 4 *ev* energy is given out. In Table 4.1 we present electronegativity data of some elements.

Periodicity of electronegativity may be expressed as under :

1. In a periodic group electronegativity decreases with increasing atomic number. As the atomic number increases new quantum shells are added. This leads to an increase in size of the atoms and also the electron dragging power of the positive nucleus decreases due to the screening effect of the inner orbital electrons (cf. Table 4.1)

2. Along a period of the table electronegativity increases with increasing atomic number. In a series of representative elements along a period electrons are being added to the same quantum shell. This does not add to the size— instead there is a slow contraction. Therefore the positive nucleus has a better scope to attract electrons from neighbouring atoms.

Electronegativity concept is one of utmost importance. (1) It helps us to predict the polarity in a molecule. The larger the electronegativity difference the greater will be ionic character of the molecule formed. (2) It helps us, as indicated above, to predict the ability of elements to attract electrons. (3) It helps us to predict which lone pair of electrons associated with hetero-diatomic ligands, such as CO, NO will function as donor in metal complexes. For example in $Ni(CO)_4$ it is the carbon lone pair that is donated to nickel (0) since oxygen being more electronegative holds its own lone pair on to itself.

Table 4.1. Electronegativities of some elements (H 2.1 ; F 4.0)

Period→	I	II	III	IV	V	VI	VII
Group ↓	Li	Be	B	C	N	O	F
	1.0	1.5	2.0	2.5	3.0	3.5	4.0
	Na	Mg	Al	Si	P	S	Cl
	0.9	1.2	1.5	1.8	2.1	2.5	3.0
	K	Ca	Ga	Ge	As	Se	Br
	0.8	1.0	1.5	1.8	2.0	2.4	2.8
	Rb	Sr	In	Sn	Sb	Te	I
	0.7	1.0	1.7	1.8	1.8	2.1	2.5

These values refer to common oxidation states. Electronegativity increases with increase in oxidation state because of enhanced positive charge.

4.5. IONIC RADIUS

It is rather difficult to offer a definition of ionic radius — instead its significance may be highlighted. An ionic radius may be assigned to an ion such that it can be added to the radius of any other ion to give the observed internuclear distance in an ionic crystal. Thus the usually accepted ionic radii of sodium ion and chloride ion are respectively 0.95A and 1.81A. The internuclear distance thus obtained is 2.76A while the actual experimental value is 2.81A. Ionic radii are of two types : (a) cationic radius and (b) anionic radius. The following periodicity in variation of these radii are observed :

1. In any group the cationic radii increase with increasing atomic number. This is obvious because size of the atoms increases down the group :

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

2. In a group the anionic radii also increase with increase in atomic number :

$$F^- < Cl^- < Br^- < I^-$$

3. Along a period similarly charged cations or anions are not available for comparison.

4. Compared to neutral atoms cationic radius is smaller while anionic radius is much larger : $Na^+ < Na$; $Cl^- > Cl$

5. Cationic radius decreases with increasing over-all charge on the cation :

$$Fe\ (1.26A) > Fe^{2+}\ (0.75A) > Fe^{3+}\ (0.60A)$$

6. Comparison of isoelectronic monopositive cation and mononegative anion, such as Na^+ and F^-, K^+ and Cl^- the reveals that negative ion is always the larger. This is because the anion has a smaller nuclear charge and hence an expanded orbital. Table 4.2 records some relevant radii.

Table 4.2. Atomic (covalent) and ionic radii (1A = 10^{-8} cm)

Atom/cation	Radius (A)	Atom/anion	Radius (A)
Na	1.86	H	0.37
Na^+	0.95	H^-	2.08
K	2.31	F	0.64
K^+	1.33	F^-	1.36
Mg	1.60	Cl	0.99
Mg^{2+}	0.65	Cl^-	1.81
Rb^+	1.48	Br	1.14
Cs^+	1.69	Br^-	1.95
		I	1.33
		I^-	2.16

4.6. LANTHANIDE CONTRACTION

In the earlier section we have noted that along a group of the periodic table cationic radii increase with increasing atomic number. This is due to the addition of new quantum shells appearing in the elements. This, however, is not the case with lanthanum and the 14 other elements following lanthanum. The lanthanides, as we have seen in section 1.8, are inner transition elements and are allotted one position in group IIIA. In their trivalent cations the 4*f* level is gradually filled up from cerium (III) to lutecium (III). This 4*f* sublevel is protected by two outer sublevels $5s^2$ and $5p^6$. Electron addition to a deep-seated inner level cannot add to the size of the ion—instead it leads to a distinct and gradual contraction of size with increase in atomic number. The added protons in the nucleus force a contraction in size of the elements of the same group. This contraction is known as lanthanide contraction. Table 4.3 gives some relevant data on some representative elements and lanthanides.

Table 4.3. Ionic Radii of Some Representative Elements and Lanthanides

Atom/Ion	Atomic Number	Electron distribution	Cationic Radius (A)
Li	3	[He] $2s^1$	Li^+ ; 0.60
Na	11	[Ne] $3s^1$	Na^+ ; 0.95
K	19	[Ar] $4s^1$	K^+ ; 1.33
Rb	37	[Kr] $5s^1$	Rb^+ ; 1.48
Cs	55	[Xe] $6s^1$	Cs^+ ; 1.69
La^{3+}	57	[Pd] $4f^0 5s^2 5p^6$	La^{3+} ; 1.06
Ce^{3+}	58	[Pd] $4f^1 5s^2 5p^6$	Ce^{3+} ; 1.03
Pr^{3+}	59	[Pd] $4f^2 5s^2 5p^6$	Pr^{3+} ; 1.01
Sm^{3+}	62	[Pd] $4f^5 5s^2 5p^6$	Sm^{3+} ; 0.96
Gd^{3+}	64	[Pd] $4f^7 5s^2 5p^6$	Gd^{3+} ; 0.94
Ho^{3+}	67	[Pd] $4f^{10} 5s^2 5p^6$	Ho^{3+} ; 0.89
Tm^{3+}	69	[Pd] $4f^{12} 5s^2 5p^6$	Tm^{3+} ; 0.87
Lu^{3+}	71	[Pd] $4f^{14} 5s^2 5p^6$	Lu^{3+} ; 0.85

4.7. ATOMIC/COVALENT RADII

Atomic or covalent radius of a nonmetal element may be defined as half the internuclear distance of its diatomic molecule. For metallic elements also the internuclear distance in the metallic crystal is determined by X-ray diffraction and is divided by two to get the atomic radius. The following periodic trends are noted with atomic/covalent radii :

1. Along a group atomic/covalent radii increase with increasing atomic numbers :

Group VIIB	:	F	Cl	Br	I
Atomic/covalent radii (A)	:	0.64	0.99	1.14	1.33

This evidently is connected with addition of electrons in new quantum shells.

2. Along a period there is a decrease in atomic/covalent radii with increasing atomic numbers. This is obviously due to the fact that no new quantum shells appear. Hence the increasing number of the protons leads to a contraction.

Period II	:	Li	Be	B	C	N	O	F
Atomic/covalent radii (A)	:	1.52	1.11	0.88	0.77	0.70	0.66	0.64

4.8. SUMMING UP

With increasing atomic number in a group in the periodic table the following changes occur :

1. Ionisation potential decreases
2. Electron affinity decreases
3. Electronegativity decreases
4. Radii of similarly charged cations increase
5. Radii of similarly charged anions increase
6. Atomic/covalent radii increase

With increasing atomic number in a period of the table the following changes occur :

1. Ionisation potential increases
2. Electron affinity increases
3. Electronegativity increases
4. Radii of similarly charged cations decrease
5. Radii of similarly charged anions decrease
6. Atomic/covalent radii decrease

EXERCISES

1. Mention some of the fundamental properties which are dependent on the position of the elements in the periodic table and show how they vary along a group and a period of the table.

2. For *every* atom, less energy is needed to remove one electron from the neutral atom than that needed to remove another electron from the resulting ion. Explain the statement.

3. What is ionisation potential? How does it vary as we move down a group and along a period of the periodic table? Discuss how this property can help us in appreciating the variations in properties of the elements of a particular group.

4. Discuss the difference between electron affinity and electronegativity. Two elements A and B of different electronegativities form a covalent compound AB. Will the compound be polar in nature?

5. We have a series of ions M^{2+}, M^{3+} and M^{4+}. Which one will exhibit the highest electronegativity?

6. Explain the relation between bond length and bond multiplicity.

7. Which of the following ones in the respective pairs has the larger radius and why?

Na, Na^+ ; Na, Cs ; H, H^- ; Cl, Cl^-

8. How does the covalent radius change as we move from lithium to fluorine or from fluorine to iodine?

9. Explain the factors which influence the ionisation potentials of elements. Cite examples in support of your answer.

10. The ionisation potential of neon is 21.56 *ev* while that of the next element sodium is only 5.14 *ev*. Explain.

CHAPTER 5

THE CHEMICAL BOND

5.1. PRELIMINARIES

Chemical Bond : *Two or more atoms of the same element or different elements can interact to give polyatomic species of energy lower than that of the interacting units. When such polyatomic species of lower energy exist we say chemical bonds hold the interacting atoms.*

Bond Energy : When atoms interact to give polyatomic species a certain amount of energy is released. This same amount of energy will evidently be required to break the polyatomic species. This energy is known as the bond dissociation energy or simply bond energy. *Bond energy may be defined as the energy required to be supplied to the molecule (or the polyatomic species) to break the bond in the gas state i.e. to take the interacting atoms to infinity.* Bond energy of H_2 molecule is 104K Cal/mole. This means 104K Cal/mole of energy has to be supplied to one gram mole of hydrogen in order to separate the interacting hydrogen atoms. The larger the bond energy the stronger is the bond.

Bond Length : *Bond length is the average internuclear distance between two atoms in a molecule.* (The term 'average' has been used because the bonded atoms are always vibrating so that the distance between the atoms is not fixed for all time—but an average distance can be determined by modern experimental techniques). The bond lengths of Cl_2 and I_2 are 1.98 and 2.66A respectively.

Bond Angle: Most often we come across polyatomic species made up of three or more atoms. *The angle that two bonding atoms makes at a central atom is called the bond angle.* Thus the bond angle in H_2O is 104°. This means that the angle formed by the two H—O bonds at the oxygen atom is 104°. Bond angle in CH_4 is 109°. This tells us that the angle any two H—C bonds make at the carbon atom is 109°.

Valence: In the good olden days in 1850 valence was defined as the combining capacity of an element. In those days valence of an element was decided by the number of atoms of hydrogen or chlorine with which an atom of the element concerned combined. Today this definition is but a historical curiosity. Since we now know so much about the electronic structure of matter that this old and primitive definition is no longer used. Since extranuclear electrons are the real key to chemical reactions we define valence in terms of electrons. Valence of an element is now defined as the number of electrons that participate during the formation of a compound.

Valence Electrons: *These are the electrons which are most loosely held by atom.* Hence these are also the electrons which are the most reactive. These electrons participate in chemical reactions. Since some elements show variable valence it follows that the number of valence electrons is not fixed for elements. Depending on the nature of reactions different number of electrons may be utilised for valence purpose.

Classification of bond types : In chemistry we come across three major bond types : (1) ionic bond (2) covalent bond and (3) metallic bond. Of these three bonds covalent bond will consume the maximum space. Under covalent bond we shall make some limited discussion on hybridisation of orbitals, molecular geometry, Fajans' rules, coordinate covalence, polarity of bonds, hydrogen bond and intermolecular forces.

5.2. IONIC BOND

This type of bond is usually found in the compound formed as a result of interaction of strongly electropositive elements with strongly electronegative elements. Compounds like NaCl, CsCl, LiF are good examples. *Ionic bond may be defined as the electrostatic force that holds together oppositely charged ions formed as a result of transfer of one or more electrons from one atom to another.*

Let us make a beginning with the metal lithium, an electropositive element, and the non-metal fluorine—a strongly electronegative element. The electron distributions of lithium and fluorine are $1s^2 2s^1$ and $1s^2 2s^2 2p^5$ respectively. A scrutiny shows that the lithium atom has just one electron more than the stable electronic configuration of the noble gas helium. On the other hand the fluorine atom has one electron short of the stable electronic configuration of the noble gas neon. The inactivity of the noble gases has been attributed to their s^2 or s^2p^6 electron arrangement. Chemical reactions occur because of interaction among the valence electrons of the combining atoms. Since the noble gas electronic configurations are very stable, all interacting atoms tend to respond so that they can attain the electronic configuration of the nearest noble gas. It follows therefore that lithium will tend to lose its single valence electron while fluorine will eagerly accept that electron. This way both lithium and fluorine can attain the respective nearest noble gas electronic configurations. However transfer of one electron from lithium will generate a monopositive lithium cation while acceptance of that electron by fluorine will produce a fluoride anion. Now a strong electrostatic force of attraction will ensue between the two oppositely charged ions. Thus an ionic bond will hold together the lithium ion and a fluoride ion. Ionic bond is sometimes referred to as electrostatic bond.

$$\text{Li} \; \underset{1s}{\underline{\uparrow\downarrow}} \; \underset{2s}{\underline{\uparrow}} \; ; \quad \text{Li}^+ \; \underset{1s}{\underline{\uparrow\downarrow}} \quad [\text{He electronic configuration}]$$

$$\text{F} \; \underset{1s}{\underline{\uparrow\downarrow}} \; \underset{2s}{\underline{\uparrow\downarrow}} \; \underset{2p}{\underline{\uparrow\downarrow}} \; \underset{2p}{\underline{\uparrow\downarrow}} \; \underset{2p}{\underline{\uparrow}}$$

$$\text{F}^- \; \underset{1s}{\underline{\uparrow\downarrow}} \; \underset{2s}{\underline{\uparrow\downarrow}} \; \underset{2p}{\underline{\uparrow\downarrow}} \; \underset{2p}{\underline{\uparrow\downarrow}} \; \underset{2p}{\underline{\uparrow\downarrow}} \quad [\text{Ne electronic configuration}]$$

It can be guessed that the factors responsible for low ionisation potential and high electron affinity will facilitate formation of ionic compounds. These factors are :

1. large size of the electropositive atom

2. low charge on the electropositive ion
3. small size of the electronegative atom
4. low charge of the electronegative ion

A consideration of all these factors allow us to predict that reactions between the alkalies/alkaline earths and the halogens are most likely to produce ionic compounds.

When one or more electrons are transferred from a metal to a nonmetal the electrons in the orbitals of the non-metals must have their spins opposed to each other—otherwise Pauli exclusion principle will be violated.

Lattice Energy : An ionic compound is an assemblage of oppositely charged ions. Each of the charged ions attracts as many of the oppositely charged ions as possible around itself. Thus structure determination has revealed that in NaCl each sodium ion is surrounded by as many as six chloride ions and vice versa. Assemblage of oppositely charged ions forms what is called a lattice. During the formation of an assemblage of oppositely charged ions energy is liberated. Conversely energy will have to be supplied in order to break down a crystal lattice. *Ionic crystal lattice energy, simply called lattice energy, may be defined as the energy liberated during the formation of the ionic crystal lattice by the oppositely charged ions in the gas phase.* The larger (the more negative) the lattice energy the stabler the ionic compound. It may be guessed that the ionic bond length will be an important factor in determining the magnitude of the lattic energy, provided the compounds compared have the same charge on their cations and anions. Table 5.1 records some relevant data of compounds containing monopositive alkali ions and mononegative halide ions.

Table 5.1. Ion distance and Lattice Energy

Compound	Cation-anion distance	Lattice energy
CsF	3.00A	– 175 KCal/mole
CsCl	3.56	– 150
CsBr	3.71	– 143
CsI	3.95	– 135

If the charge on the cation and the anion increases the lattice energy will go up considerably. Thus the lattice energies of MgO, CaO, SrO and BaO are –940, –842, –791 and –747 KCal/mole respectively. At this stage we should have enumerated the important properties associated with ionic compounds. But these can be properly appreciated alongside the properties arising out of covalent bonding. So we shall take up this subject at the appropriate place.

5.3. COVALENT BOND

Ionic bonds are formed between atoms of very different characters. One interacting atom must have low ionisation potential and low electron affinity while the other atom must have high values for I.P. and E.A. But then what happens in diatomic molecules like H_2, Cl_2, N_2 or molecules like H_2O and NH_3? In the diatomic molecules the interacting atoms are the same and hence have the same I.P. and E.A. The situation of complete transfer of one electron from hydrogen to the second hydrogen is just unthinkable. But H_2 is a reality. We have already seen that the clue to chemical interaction is the desire to attain noble gas configuration by the interacting atoms. Here too, noble gas configuration can be attained provided both the interacting atoms allow a mutual sharing of an electron pair. *A covalent bond may be defined as one where equal sharing of valence electrons takes place.*

Let us look at the hydrogen molecule little seriously. Both the interacting hydrogen atoms have their valence electron in their 1*s* orbital. If these two electrons are to be equally shared the two atoms must come closer so that there can be an interaction between the electrons. Such an interaction will necessarily mean that the two orbitals overlap each other and then coalesce into one – that will be common to both the atoms. It also follows that in order to have two electrons in one and the same orbital Pauli exclusion principle has to be obeyed. The principle states that no two electrons of the same atom can have all the four quantum numbers the same. The only way the situation can be saved is by having opposing spins in the two electrons. To start with both the 1*s* electrons of the two hydrogen atoms have the same value for n (= 1), l (= 0) and m_l (= 0). *Therefore fruitful overlap of orbitals and hence sharing of electron pair is possible if the interacting electrons have opposite spins.*

The essential condition that we have mentioned above gives us a fine tool to explain why the noble gases are monatomic. Take for example the case of helium. Its electronic configuration is $1s^2$ which is a closed, saturated shell. The two 1*s* electrons have already their spins opposite to each other. Therefore there is no motivation on the part of two helium atoms to come closer to allow an overlap of their orbitals.

5.3.1. Single Bond, Double Bond and Triple Bond. In diatomic hydrogen molecule the two 1*s* orbitals overlap. The interacting electrons have their spins opposed i.e. antiparallel. The resulting orbital is concentrated in between the two hydrogen nuclei. In the H_2 molecule there is more electron density in between the nuclei compared to the non-interacting situation. One can argue that there will be electron proton attraction but then there will also be electron-electron and proton-proton repulsion. In reality it is observed that when the internuclear distance is 0.74A, as is the case for H_2, the two electrons are quite able to overcome the nuclear proton repulsion. The oppositely charged electrons serve as binding material by minimising the nuclear Coulomb repulsion. In Cl_2 molecule two *p* orbitals with one unpaired electron on each overlap to form the diatomic molecule. In these cases the overlap of the orbitals takes place along the internuclear bond axis. Electron density is symmetrically distributed all around the bond axis. *Such a bond where the electron density is symmetrically distributed all around the bond axis is known as a sigma* (∂) *bond.* In H_2O molecule there are two sigma bonds between oxygen and the two hydrogen atoms. In H_2, Cl_2 there is but one sigma bond. These molecules afford examples of single bond between the interacting atoms. Single bonds are usually represented with a dash between the interacting atoms : H–H ; Cl–Cl ; H–O–H etc.

In double or triple bonds there are two or three bonds in between two interacting atoms. C_2H_4 (ethylene) and C_2H_2 (acetylene) are examples of a double bond and a triple bond, respectively, between the two interacting carbon atoms. The very simple orbital overlap idea developed above cannot explain the molecular structure with multiple bonds. One interesting tool that has been handed down to us by Linus Pauling to tackle problems of multiple bonding is the concept of hybrid orbitals.

Hybridisation of Atomic Orbitals: Let us take the case of carbon. We know that the ground state electron distribution of carbon (atomic number 6) is $1s^2 2s^2 2p^1 2p^1$. Our simple rule of covalent bonding will predict that carbon can only be bivalent since it has only two unpaired electrons. However our experience shows that it is almost always quadri-covalent. This means we have to have as many as four reactive electrons i.e. we must produce four valence electrons. This we can do by taking carbon from its ground state to the following excited state :

$$\text{carbon (ground state)} : \quad \underset{1s}{\underline{\uparrow\downarrow}} \quad \underset{2s}{\underline{\uparrow\downarrow}} \quad \underset{2p}{\underline{\uparrow}} \quad \underset{2p}{\underline{\uparrow}} \quad \underset{2p}{\underline{}}$$

$$\text{carbon (excited state)} : \quad \underset{1s}{\underline{\uparrow\downarrow}} \quad \underset{2s}{\underline{\uparrow}} \quad \underset{2p}{\underline{\uparrow}} \quad \underset{2p}{\underline{\uparrow}} \quad \underset{2p}{\underline{\uparrow}}$$

Now we do have four reactive valence electrons but we can easily see that their orientation in space is different. Three *p* orbitals are on the three cartesian axes while the *s* orbital is spherically symmetrical with no preference for any orientation. So even if carbon now forms four covalent bonds these bonds will not be equivalent. In reality we do find that the four bonds that carbon forms in CH_4 or CCl_4 are equivalent with bond angles of 109°. Pauling demonstrated with the help of quantum mechanics that pure atomic orbitals may be mixed to generate mixed or hybrid orbitals. The relative orientation of the hybrid orbitals is different from that in the pure atomic orbitals.

1. Mixing of one *s* and one *p* orbitals gives two equivalent hybrid orbitals concentrated along the axis of the particular *p* orbital chosen. Note *s* orbital is spherically symmetrical and hence this orbital is drawn along the particular cartesian axis of the *p* orbital. These two atomic orbitals give two *sp* hybrid orbitals (Fig 5.1).

2. Mixing of the *s* orbital with the two *p* orbitals lying in the same plane (say, p_x and p_y) will generate three equivalent sp^2 hybrid orbitals. Since the two *p* orbitals are on the same plane and the *s* orbital has no directional preference the three hybrid orbitals will lie on the same *xy* plane. In order to maintain equivalence the three hybrid orbitals will be planar with an angle of 120° (Fig 5.1).

3. Combining one *s* and three *p* orbitals produce four new equivalent hybrid sp^3 orbitals. Each of these four hybrid orbitals points towards an apex of a regular tetrahedron. The angle between these hybrid orbitals is 109° (Fig 5.1).

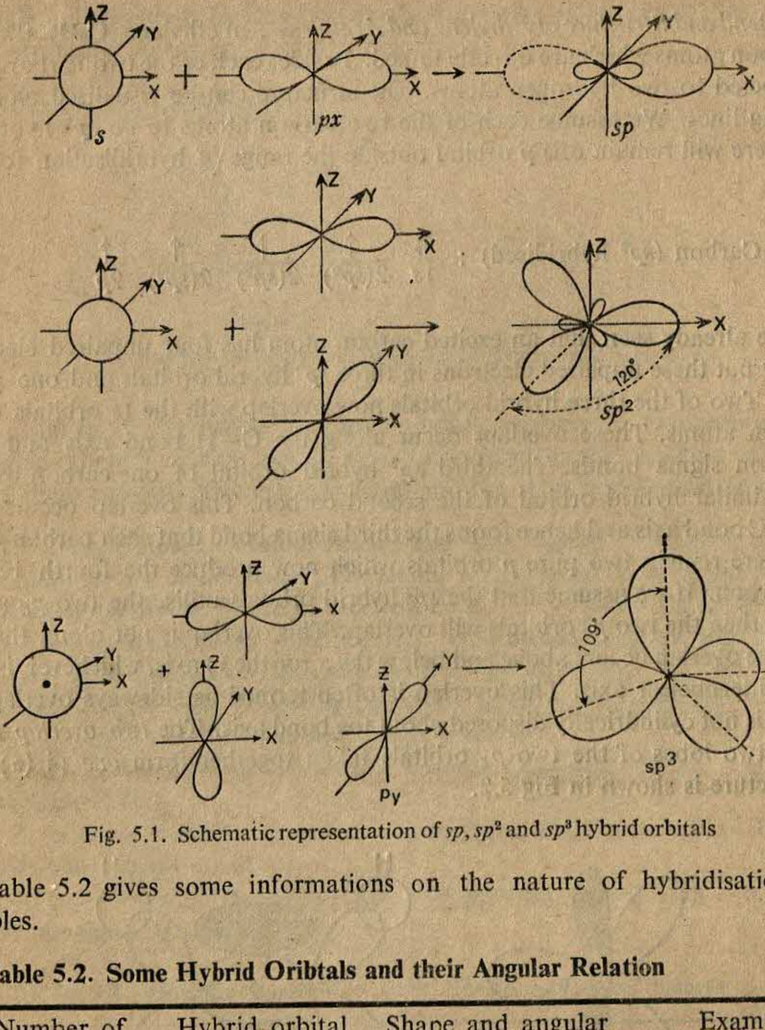


Fig. 5.1. Schematic representation of sp, sp^2 and sp^3 hybrid orbitals

Table 5.2 gives some informations on the nature of hybridisation with examples.

Table 5.2. Some Hybrid Oribtals and their Angular Relation

Number of Covalent bonds	Hybrid orbital	Shape and angular relation	Example
2	sp	Linear (180°)	$HgCl_2$ $Hg(CH_3)_2$ $[Ag(NH_3)_2]^+$
3	sp^2	Triangular planar (120°)	BCl_3, BF_3
4	(a) sp^3 (b) dsp^2	Tetrahedral (109°) Square planar (90°)	CH_4, $[BF_4]^-$ $[PtCl_4]^{2-}$
6	(a) d^2sp^3 (b) sp^3d^2	(a) Octahedral (b) Octahedral	(a) $[Co(NH_3)_6]^{3+}$ (b) SF_6

Pi Bond and Structure of Ethylene and Acetylene : In ethylene, C_2H_4, there are two carbon atoms which are directly linked. Besides each of the two carbon atoms is connected to two hydrogen atoms. The structure can be visualised along the following lines. We assume each of the two carbon atoms to be sp^2 hybridised. Then there will remain one p orbital outside the range of hybridisation for each carbon.

Carbon (sp^2 hybridised) : $\underset{1s}{\uparrow\downarrow}$ $\underset{2(sp^2)}{\underline{\uparrow}}$ $\underset{2(sp^2)}{\underline{\uparrow}}$ $\underset{2(sp^2)}{\underline{\uparrow}}$ $\underset{2p}{\underline{\uparrow}}$

We have already seen that an excited carbon atom has four unpaired electrons. We now put these unpaired electrons in three sp^2 hybrid orbitals and one pure p orbital. Two of the three hybrid orbitals now overlap with the $1s$ orbitals of two hydrogen atoms. These overlaps occur along the C—H bond axis and hence they form sigma bonds. The third sp^2 hybrid orbital of one carbon overlaps with a similar hybrid orbital of the second carbon. This overlap occurs along the C—C bond axis and hence forms the third sigma bond that each carbon forms. Now there remain two pure p orbitals which now produce the fourth bond of each carbon. If we assume that the sp^2 hybrid orbitals utilise the two p_x and p_y orbitals then the two p_z orbitals will overlap. This overlap is not along the bond axis. The overlap occurs above and below the x (or the y) axis, whichever is taken as the internuclear axis. This overlap is often termed as sideways overlap. The overlap is not cylindrically disposed about the bond axis. The *two overlap regions* for the two lobes of the two p_z orbitals taken together form *one* pi (π) bond. The sructure is shown in Fig 5.2.

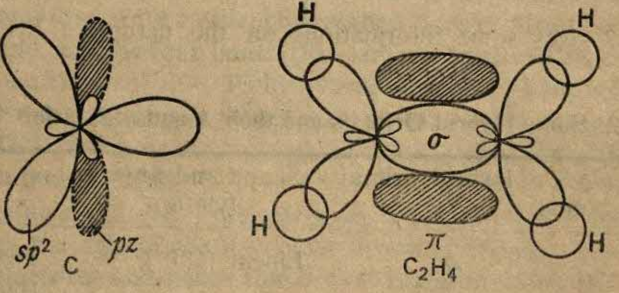
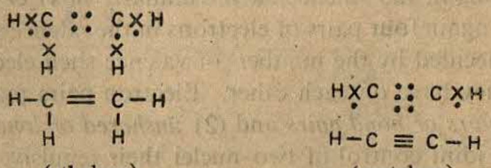


Fig. 5.2. Pi bond and structure of ethylene

In acetylene, C_2H_2, there are two carbon atoms which are directly linked. Each of the two carbon atoms is bonded to one hydrogen atom only. In this case we have to assume that each of the two carbon atoms is sp hybridised. So the four electrons of the excited carbon atom are now placed in the two sp hybrids and in the two remaining pure p orbitals. One sp hybrid makes an overlap with one $1s$ orbital of one hydrogen while the other sp hybrid overlaps with one sp hybrid of the other carbon atom. If we assume that the p_x orbital is involved in the hybridisation then the two p_y orbitals make sideways overlap to make one pi (π) bond. Similarly a second pi bond is formed by the overlap of the p_z orbitals. The structural forms are shown in Fig 5.3.

Carbon (*sp* hybridised) : $\underset{1s}{\uparrow\downarrow}$ $\underset{2(sp)}{\uparrow}$ $\underset{2(sp)}{\uparrow}$ $\underset{2p}{\uparrow}$ $\underset{2p}{\uparrow}$



(ethylene) (acetylene)

Fig. 5.3. Pi bonds and structures of ethylene and acetylene

Note that in ethylene there is a double bond between the two carbons while in acetylene there is a triple bond. Also to be noted is the fact that in a multiple bond there can only be one sigma bond and the other bonds must be pi bonds.

5.3.2. Multiple Bond, Covalent Radius and Bond Energy. In multiple bond the interacting atoms come closer. The sigma and pi bonds help reduce the nuclear Coulombic repulsion. More of electron density in between the nuclei functions as a cementing material between the nuclei. Internuclear distance and consequently covalent radius decrease. This increases the binding strength and hence the bond energy (Table 5.3). The following points are worth taking care of :

1. A single bond is invariably a sigma bond.
2. A double bond is composed of one sigma and one pi bond. The hybridisation involved is sp^2.
3. A triple bond is composed of one sigma bond and two pi bonds. The hybridisation involved is sp.
4. sp, sp^2 and sp^3 hybrid orbitals can generate respectively two, three and and four sigma bonds.

Table 5.3. Multiple Bonds, Covalent Radius and Bond Energy

Multiple Bond	Covalent Radius (A)	Bond Energy (KCal/mole)
$C-C$	0.77	83
$C=C$	0.66	143
$C\equiv C$	0.602	196
$N-N$	0.76	38
$N=N$	0.60	100
$N\equiv N$	0.55	225

5.3.3. Molecular Geometry on Valence Shell Electron Pair Repulsion: We have earlier noted that hybridisation of atomic orbitals can often give a good description of the molecular geometry. An alternative approach is to consider the number of electron pairs in the valence shell of the central element and the repulsion effect they exert. The number of electrons in the valence shell is given by the sum of the electrons in the outermost quantum sublevels and the electrons gained from the interacting partners. Thus nitrogen has the outer orbital electron configuration as $2s^2 2p^3$ and hence it has five electrons on the outer shell. When NH_3 is formed nitrogen has a share on the three electrons coming from the three hydrogen atoms. So the valence shell electrons of nitrogen in NH_3 are eight i.e. it has *four pairs* of electrons in the valence shell. Similarly in H_2O oxygen has 6 plus 2 i.e. 8 electrons i.e. again four pairs of electrons in the valence shell. The geometry of the molecule is decided by the number of valence shell electron pairs and the mutual repulsion they have on each other. Electron pairs may again be of two types : (1) *shared pairs or bond pairs* and (2) *unshared or lone pairs.* Since bond pairs are under the joint control of two nuclei their repulsive effect is less than that of lone pairs which is controlled by one nucleus only.

Electrons repel each other. *A stable geometry results only when electron pair repulsion becomes minimum.* Let us take the case of two valence shell electron pairs. These two pairs will attain minimum repulsion condition when they are positioned at 180° to each other. In other words the geometry of a compound with the central element having two electron pairs is expected to be linear. In fact in $HgCl_2$ mercury (II) has a valence shell of two pairs and the geometry is indeed linear. In BCl_3 boron atom has a valence shell of three pairs. These three pairs can generate a stable system when the three pairs are equilateral triangular with an angle of 120° between the pairs. The geometry of BCl_3 is indeed a planar triangular one with the Cl—B—Cl angle 120°. Now let us turn to ammonia. Nitrogen in NH_3 has a valence shell of four pairs. Four pairs ideally should generate a regular tetrahedral geometry. But then we must remember that of the four pairs there is one lone pair while there are three bond pairs. The lone pair repels the three bond pairs somewhat more strongly. The result is that the ideal tetrahedral angle of 109° is squashed a little. The H—N—H angle is 107°. Three of the four corners of the tetrahedron are occupied by the three H's while the fourth is taken up by the lone pair. The molecule is therefore said to have a pyramidal structure. In CH_4 all the four electron pairs are shared pairs and hence the extent of repulsion is the same. We do get a regular tetrahedral structure. We now turn to H_2O. Here the valence shell of oxygen has four electron pairs, of which two are bond pairs and two are lone pairs. The two lone pairs repel the bond pairs severely and therefore the H—O—H angle is squashed down to 104°. We see that two apices of the tetrahedron are occupied by the two hydrogen atoms while the other two are occupied by the lone pairs. Schematic geometry with the valence shell electron pairs for the molecules CH_4, NH_3, H_2O and BCl_3 are shown in Fig 5.4.

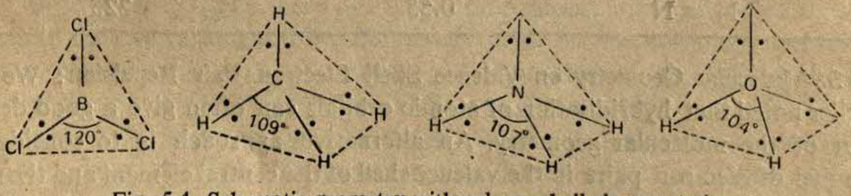


Fig. 5.4. Schematic geometry with valence shell electron pairs of BCl_3, CH_4, NH_3, and H_2O

The discussions and the results are summarised in Table 5.4.

Table 5.4. Electron Pairs in the Valence Shell and Geometric Shape

AX_n	Electron Pairs in Valence Shell	Lone Pairs	Geometry	Examples
AX_2	2	0	Linear	$HgCl_2$, $(CH_3)_2Hg$
	4	2	V shaped	H_2O
AX_3	3	0	Triangular planar	BCl_3
	4	1	Pyramidal	NH_3, $AsCl_3$
AX_4	4	0	Tetrahedral	CH_4, CCl_4
AX_6	6	2	Square Planar	XeF_4
	6	0	Octahedral	SF_6

5.4. IONIC BOND VERSUS COVALENT BOND

We have already seen that ionic compounds are formed as a result of formation of oppositely charged ions. There is a strong force of attraction between these oppositely charged ions. Each cation tends to drag as many anions as it can and vice versa. Thus in an ionic compound no single, discrete molecule exists—instead a giant molecule is a reality. On the other hand a covalent molecule is complete in itself. Since no ions are present giant molecules are not formed. There exists, however, a *weak force of attraction* in between molecules. The nature of this weak force will be discussed in short at a later stage. Table 5.5 summarises the important distinctive features of these two varieties of compounds.

Table 5.5. A Comparison of Properties of Ionic and Covalent Compounds

Characteristics	Ionic Compounds	Covalent Compounds
1. Structure	Composed of oppositely charged ions; giant molecules	No ions ; discrete molecules exist
2. Conductance	Electrical conductor in fused state and aqueous solution	Non-conductor
3. Melting point and boiling point	High	Low
4. Solubility	Soluble in polar solvents like water but insoluble in non-polar solvents	Soluble in non-polar solvents but insoluble in polar solvents
5. Rate of reaction	Fast	Slow
6. Examples	NaCl, CsCl, LiF, MgO, CaO, RbI	CH_4, NH_3, $CHCl_3$, CCl_4, $SiCl_4$, SF_6

5.5. TRANSITION BETWEEN IONIC AND COVALENT BONDS : FAJANS' RULES

So far two extreme cases of bonding, namely ionic and covalent, have been discussed. We now ask the question : Can there be no compound with intermediate properties? The answer to this pertinent question has been provided by Fajans. In the chemical world there are rather lesser number of compounds which could be classed as purely ionic or purely covalent. More often we have compounds with intermediate properties. Fajans has argued that the size and the charge of the hypothetical cation and anion are the factrors that may lead to the deformation of an ionic compound to a covalent compound. Ions are deformed when electrons from the ions are dragged out of their orbitals and are shared by the interacting atoms.

1. The greater is the charge on the cation the more it will deform the anion. The highly charged cation will drag the anion electrons.

2. The larger the charge on the anion the more difficult it is for the anion to control its electrons.

3. The smaller the size of the cation the more effective it will be in dragging out the anion electrons.

4. The larger the size of the anion the more difficult it is to keep its own electrons under control.

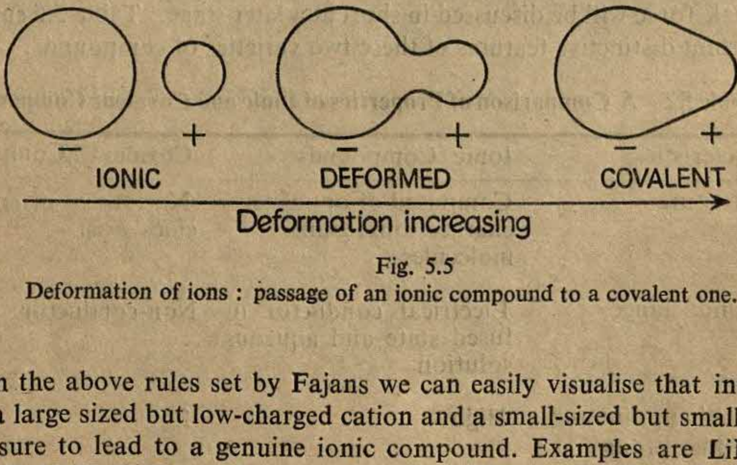


Fig. 5.5
Deformation of ions : passage of an ionic compound to a covalent one.

From the above rules set by Fajans we can easily visualise that interaction between a large sized but low-charged cation and a small-sized but small-charged anion is sure to lead to a genuine ionic compound. Examples are LiF, NaCl, CsCl, RbF, MgO, CaO etc. Compounds such as CCl_4, $SiCl_4$, SF_6, $SnCl_4$ are sure to be covalent. There are some elements which exhibit variable valence. Lower valent compounds, according to Fajans' rules, are likely to be more ionic than the higher valent compounds. Thus we find that the melting points of $PbCl_2$ and $PbCl_4$ are 501°C and −15°C respectively. We can safely conclude that lower valent $PbCl_2$ is ionic while the higher valent $PbCl_4$ is covalent. Similar conclusion can be drawn in respect of $SnCl_2$ (melting point 246°C) and $SnCl_4$ (melting point−33°C).

5.6. COORDINATE COVALENCE

In a classical covalent bond the two interacting atoms contribute one electron each and the pair is then shared jointly. In some cases a situation might arise when one interacting partner has two electrons to spare but the other partner being electron deficient has none to spare. In such a case there occurs an overlap between a filled orbital of the *donor atom* and an empty orbital of the *acceptor* atom. Such a covalent bond is an example of *coordinate covalence*. NH_3 has a lone pair of electrons in one of its sp^3 hybrid orbitals. BF_3, on the other hand, has only three electron pairs in its three hybrid sp^2 orbitals. This is an electron deficient molecule so far as a stable octet is concerned. Now NH_3 and BF_3 react vigorously to produce crystals of $F_3B \leftarrow NH_3$. The arrow indicates that nitrogen is the donor and boron is the acceptor. However once the covalent link is established it is hard to locate the donor or the acceptor. But the arrow does help us to have a pictorial view of the donation (Fig 5.6). For the young readers it may be mentioned that the above bonding gives rise to four covalent bonds about boron. Boron, which was originally three-covalent sp^2 hybridised, becomes four-coordinate tetrahedral sp^3 hybridised. According to Fajans' rules the H^+ ion being the smallest conceivable cation (a bare proton ; radius 10^{-12} cm) is most likely to have good deforming power. In fact it is so. We never find a bare proton in aqueous solution. The proton gets aquated to the form H_3O^+. Some more examples of coordinate covalence are depicted in Fig 5.7.

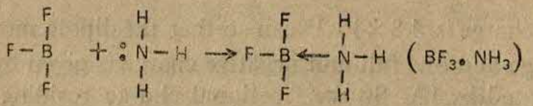


Fig. 5.6. Donor-acceptor coordinate covalence in $F_3B \leftarrow NH_3$

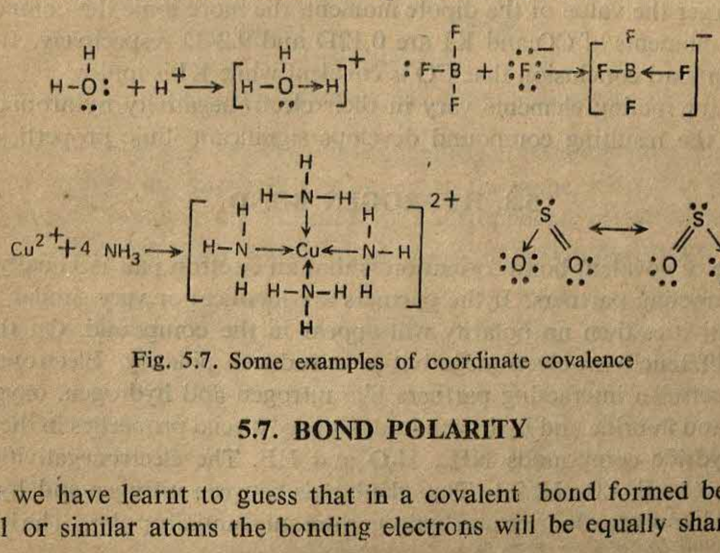


Fig. 5.7. Some examples of coordinate covalence

5.7. BOND POLARITY

By now we have learnt to guess that in a covalent bond formed between two identical or similar atoms the bonding electrons will be equally shared i.e. the bonding electrons will be symmetrically distributed about the two nuclei. If the two interacting atoms are not identical or similar then the electron distribution cannot be symmetrical ; in other words the electron pair will not be equally shared. Such a bond is called *polar covalent bond.* Polarity in a covalent bond arises whenever there is a difference in electronegativity of the two atoms.

Polarity is expressed in terms of dipole moment. If the molecule has two equal but opposite charges (δ) separated by a distance d then the product of the charge and the distance gives the dipole moment $\mu = \delta \times d$. Since the electronic charge is of the order of 4.8×10^{-10} esu and distance is in unit of 1×10^{-8} cm (A) the unit of dipole moment is 1×10^{-18} esu-cm, called 1 Debye (1D). The internuclear distance in H$-$Br is 1.42×10^{-8} cm. Its dipole moment has been found to be 0.79D. So we can calculate the magnitude of the charge located at the two ends of the molecule

$$\delta = \frac{\mu}{d} = \frac{0.79 \times 10^{-18} \text{ esu cm}}{1.42 \times 10^{-10} \text{ cm}} = 0.56 \times 10^{-10} \text{ esu}$$

A full electronic charge is 4.8×10^{-10} esu so that the dipole moment of one full unit positive charge and one full unit negative charge is given by 4.8D. when the charges are separated by 1A. So the fractional charge residing at each nucleus of HBr is :

$$\frac{0.56 \times 10^{-10} \text{ esu}}{\text{electronic charge}} = \frac{0.56 \times 10^{-10} \text{ esu}}{4.8 \times 10^{-10} \text{ esu}} = 0.11$$

Similarly the dipole moment of HCl is 1.03D. Given the bond length 1.27A, a charge of 0.81×10^{-10} esu can be calculated. This amounts to a fraction 0.17 of a full fundamental charge. These fractions of charges do indicate that a full electron has not been transferred from hydrogen to bromine or chlorine. Therefore we say that *the bond in HCl or HBr molecule is not ionic but polar covalent.*

The larger the value of the dipole moment the more ionic the compound is. The dipole moments of CO and KI are 0.12D and 9.24D respectively. It is then a straightforward conclusion that CO is covalent while KI is ionic.

If the interacting elements vary in their electronegativity by around 1.6 or more then the resulting compound develops significant ionic properties.

5.8. HYDROGEN BOND

The essence of covalent bond formation is that an electron pair is equally shared by two interacting partners. If the partners are identical or very similar in their electronegativities then no polarity will appear in the compound. On the other hand a difference in electronegativities introduces polarity. Electronegativity difference between interacting partners like nitrogen and hydrogen, oxygen and hydrogen, and fluorine and hydrogen leads to very special properties in the corresponding hydride compounds NH_3, H_2O and HF. The electronegativities are : N, 3.0 ; O, 3.5 ; F, 4.0 ; H, 2.1. Thus the bonds between nitrogen and hydrogen, oxygen and hydrogen, fluorine and hydrogen are substantially polar. The hydrogen end becomes partially positive (δ^+) while the nitrogen, oxygen or fluorine end becomes partially negative (δ^-). The partially positive hydrogen end of say HF can have some electrostatic attracting force on the fluorine end of a second HF molecule. Such interaction initiated by hydrogen leads to association of HF. Similar association takes place in H_2O and NH_3. When hydrogen is covalently bonded to a very strongly electronegative atom, it can form a second weak bond with another electronegative atom with lone pair (s) of electrons. Such interaction forced by hydrogen between two electronegative elements is called *hydrogen bond.* Fig. 5.8 gives an idea of hydrogen bonding in HF and H_2O.

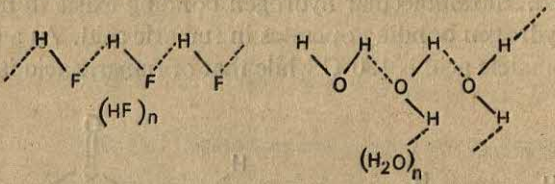


Fig. 5.8. Hydrogen bonding in HF and H_2O

As we go down the groups VB, VIB, and VIIB electronegativity falls and the strength of hydrogen bonding decreases. Thus the strength of hydrogen bonding in H_2S is far weaker than in H_2O. The result is very imposing : while H_2S, with a higher molecular weight, is a gas H_2O with a lower molecular weight is a liquid. In general the boiling points of NH_3, H_2O and HF are higher than the following hydrides of the respective groups : PH_3, H_2S and HCl.

Hydrogen bond may be of two types : intermolecular and intramolecular. *Intermolecular hydrogen bonding* : This, as the very name suggests, occurs between molecules. Good examples are NH_3, H_2O and HF as already shown above. Dimerisation of acetic acid is also another example.

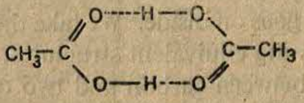


Fig. 5.9. Dimerisation of CH_3COOH due to hydrogen bonding

Intramolecular hydrogen bonding : Such hydrogen bonding can occur if suitable functional groups are properly positioned in the same molecule. Examples of such hydrogen bonding are afforded by *o*-nitrophenol, *o*-hydroxybenzaldehyde (i.e. salicylaldehyde), salicylic acid (Fig 5.10.). If the functional groups are disposed

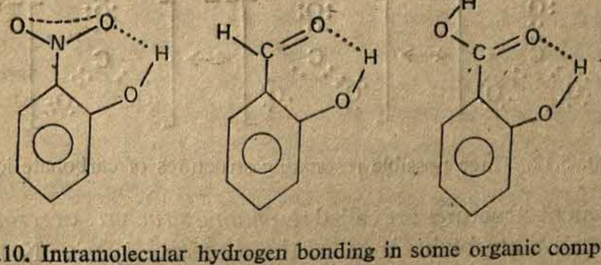
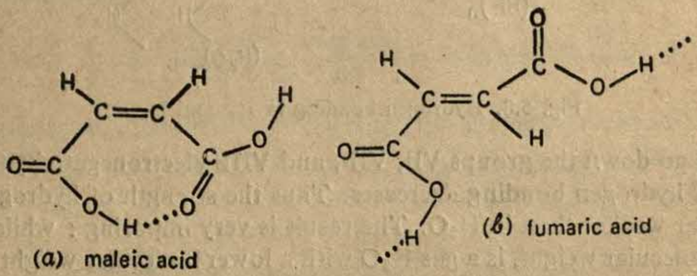


Fig. 5.10. Intramolecular hydrogen bonding in some organic compounds

meta or *para* with respect to each other, the strength of intramolecular hydrogen bonding becomes too weak. A little thought will tell us while *o*-nitrophenol can give rise to intramolecular hydrogen bonding, the para isomer can participate in intermolecular hydrogen bonding. Intramolecular hydrogen bonding is weaker than the intermolecular hydrogen bonding. This explains why the melting point of *o*-nitrophenol is 45°C while that of *p*-nitrophenol is 114°C.

Another set of compounds which offer interesting comparison are the two isomeers of HOOC—CH = CH—COOH: (a) maleic acid and (b) fumaric acid (Fig 5.11). In maleic acid the two COOH groups are *cis* while in fumaric acid they are *trans* disposed. Intramolecular hydrogen bonding exists in maleic acid while intermolecular hydrogen bonding operates in fumaric acid. As a consequence the melting point of maleic acid is 130°C while that of fumaric acid is 287°C.


(*a*) maleic acid

(*b*) fumaric acid

Fig. 5.11. Intramolecular and intermolecular hydrogen bonding in maleic acid and fumaric acid

5.9. RESONANCE

There are some multicentred molecules or ions for which we can write more than one equivalent or nearly equivalent structures. For such molecules or ions no one structure describes what goes on inside. We take the structure of the carbonate ion. We can write the following equivalent structures. In all the three structures there are two single bonds between carbon and two oxygen atoms and a double bond between one oxygen and the carbon atom. The positions of the single bonds and the double bond are interchanged. There is a sigma bond between the carbon atom and each of the three oxygen atoms. The position of the pi (π) bond changes among all the three oxygen atoms. Effectively none of the bonds is a pure single bond nor a pure double bond. On an average we can say that each of the three bonds is a 1⅓ bond—intermediate between a single bond and a double bond.

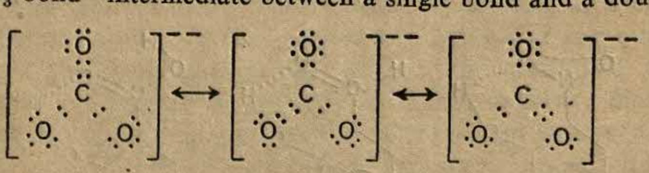


Fig. 5.12. Three possible resonating structures of carbonate ion

The equivalent structures are called *resonating structures* or *resonance notations.* The real structure that obtains is called the *resonance hybrid.* Note we can write the resonance structures but not the resonance hybrid. There are certain rules about writing the resonance structures :

1. The positions of the various atoms should remain the same.
2. The number of unpaired spins should remain the same.
3. The energies of the different structures should not vary greatly.

The contribution of the different resonance structures towards the resonance hybrid need not be the same. A two-way arrow between two structures indicates resonance. The resonance structures of CO_2 and benzene are shown in Fig 5.13. In benzene, as we are familiar, the single bonds and the double bonds change positions among themselves.

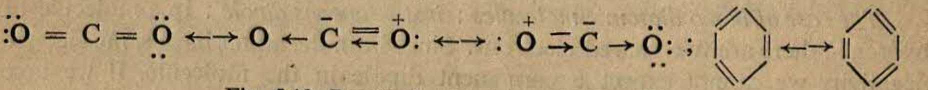


Fig. 5.13. Resonating structures of CO_2 and benzene

5.10. METALLIC BOND

Explanation of the bonding that holds together atoms of metals is rather complicated. In a metal crystal all the metal atoms are identical. All the atoms have the same low ionisation potential and low electron affinity. This means the metal atoms are not quite ready to share electron pairs. That is, metals are not likely to form covalent bonds. The modern approach to bonding in metals is a modification of the multicentred bonding we have talked of earlier.

Atomic orbitals can be conceived to combine among them to give molecular orbitals. The molecular orbitals belong to the molecule as a whole, and not to any particular atom. N number of atomic orbitals generate N number of molecular orbitals. Half of these molecular orbitals i.e. $\frac{1}{2}N$ form the bonding molecular orbitals of energy lower than those of the combining atomic orbitals. The other $\frac{1}{2}N$ molecular orbitals are of higher energy than the atomic orbitals. Available electrons occupy the lower energy molecular orbitals following Pauli exclusion principle. Formation of Li_2 will require formation of two molecular orbitals from the combination of the two $2s$ atomic orbitals. The only bonding molecular orbital will be filled up by the two electrons coming from the two lithium atoms. Following Pauli exclusion principle the two electrons will pair their spins in the bonding molecular orbital. This approach can be extended to many more metal atoms. Just as $2s$ atomic orbitals have been conceived to have generated molecular orbitals, similarly $2p$ orbitals can also generate molecular orbitals, which will not be much different in energy than the former molecular orbitals. Such molecular orbitals will be able to bind many nuclei together. In essence the outermost orbitals of the free metal atoms are converted to multicentre molecular orbitals whose energies are quite close. These closely spaced orbitals are known to form *valence band.*

On the passage of electricity some of the electrons from the bonding molecular orbitals are raised to the antibonding orbitals and thus conduct electricity.

5.11. NATURE OF INTERMOLECULAR ATTRACTION

We have once mentioned that a covalent molecule is complete in itself. There exists only a weak force of attraction in between such molecules. We now ask ourselves two questions : (1) what is the evidence that there is intermolecular attraction between covalent molecules? (2) if there is intermolecular attraction what is its origin?

It is our practical experience that gaseous elements like hydrogen, oxygen, etc or compounds like HCl (gas), H_2S etc can be liquified. Then again these gaseous elements or compounds are made of covalent bonds. Since these can be liquified it means there must be some force of attraction in between the molecules, which increases with lowering of temperature finally giving the liquid state.

There are several origins of the intermolecular forces. In this elementary text we shall discuss only the two most important cases.

The case of homo diatomic molecules : *instantaneous dipole* : In a molecule of hydrogen there are two shared electrons. Since both the atoms have same electronegativity we cannot expect a permanent dipole in the molecule. If we take the case of two neighbouring H_2 molecules then the electrons will so correlate their movement that electrostatic repulsion will be minimised (Fig 5.14). When the pairs of electrons are close to each other there will be a strong repulsion. But when one of the pairs is on the far side of one molecule while the other pair is close to one of the nuclei of the first molecule there will result an instantaneous dipole in a H_2 molecule. This instantaneous dipole will induce instantaneous dipoles in neighbouring molecules. This is the clue to liquefaction of gases like H_2, O_2, etc.

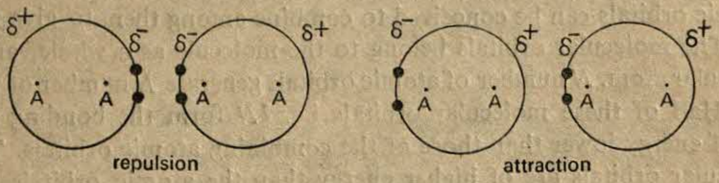


Fig. 5.14. Formation of instantaneous dipoles in a molecule AA

The case of hetero diatomic molecules : *permanent dipoles* : An understanding of the nature of the intermolecular forces in molecules like, HCl, ICl, etc is quite straightforward. The molecules are made up of atoms with different electronegativities. As a result there develops a permanent dipole in such molecules. For example in HCl, the (δ^+) positive hydrogen end will attract the (δ^-) negative end of a second HCl molecule. The (δ^-) negative chlorine end of one molecule will drag the (δ^+) positive hydrogen end of a second molecule. This eventually will get stronger as the temperature is lowered, leading to liquefaction.

These weak intermolecular forces are together termed as van der Waals forces. Note the gas equation has a correction due to such forces.

EXERCISES

1. Pick up one typical ionic compound and another typical covalent compound and discuss the differences in their properties.

2. There are two elements A and B. A has a low first ionisation potential while B has a very high electron affinity. What will be the kind of the compound AB?

3. What do you understand by chemical bond? Give the major classifications of chemical bonds with their meanings and associated properties.

4. Which of the following compounds are likely to show hydrogen bonding :

CH_4 ; H_2O ; H_2S ; PH_3 ; NH_3 ; HF ; HI.

The electronegativities are : C, 2.5 ; H, 2.1 ; O, 3.5 ; P, 2.1 ; N, 3.0 ; F, 4.0 and I, 2.5

5. Is it correct to say that NaCl is a polar compound?

6. Present a qualitative idea of hybridisation in CH_4 and BCl_3.

7. What is the difference between sigma and pi bonds?

8. Discuss the electron arrangement and the bondings in CO, SO_2 and CCl_4.

9. What is resonance? Can we write down the resonance hybrid structure of a compound?

10. Discuss Fajans' rules of deformation of ions. In this context explain the bond types in the following compounds :

CCl_4, $SnCl_2$, $SnCl_4$, CO_2, NaCl, CsBr, BF_3

11. Give an account of hydrogen bonding. Explain why H_2S with a higher molecular weight is a gas while H_2O with a lower molecular weight is a liquid.

12. How many sigma and pi bonds are there in a single, double and a triple bond?

13. Use valence shell electron repulsion theory to predict the shapes of the following compounds :

CH_4, BF_3, H_2O, $HgCl_2$

14. Write short notes on :

(*a*) resonance (*b*) dipole moment (*c*) van der Waals' forces (*d*) coordinate covalence (*e*) metallic bond (*f*) structures of ethylene and acetylene.

CHAPTER 6

COORDINATION CHEMISTRY

6.1. ALFRED WERNER LAYS THE FOUNDATION STONE

Way back in 1798 Tassaert carried out a reaction between cobalt chloride hexahydrate, $CoCl_2.6H_2O$, and aqueous ammonia. On leaving the reaction mixture overnight he obtained some orange coloured crystals. On analysis the crystals appeared to have a composition $CoCl_3.6NH_3$. This compound went unnoticed for nearly a century. It was in 1890's that a chemical luminary Alfred Werner got interested in the structure of $CoCl_3.6NH_3$ and similar other compounds.

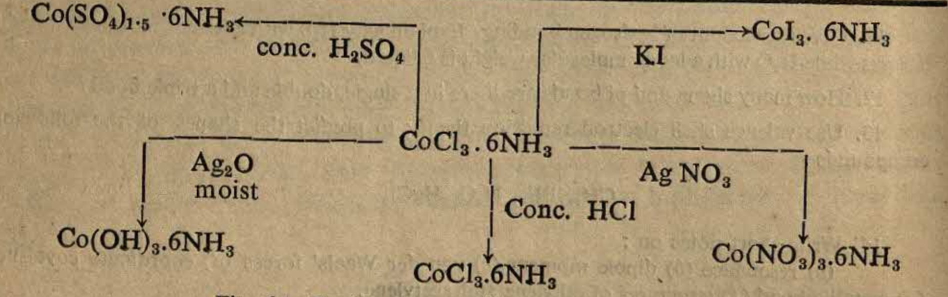


Fig. 6.1. Double decompositions on $CoCl_3.6NH_3$

Chemists in those days had no conception about the possible structure of these compounds. Werner in his own way carried out several double decompositions on this compound of Tassaert (Fig 6.1). The major and startling finding of these studies was that in these double decomposition reactions only the three chloride units were replaced by other anions. Cobalt and the six ammonia groups remained intact. From these results on $CoCl_3.6NH_3$ and some more similar compounds Werner proposed his *coordination theory*. The major aspects of the theory are :

1. *A metal ion is surrounded by certain number of neutral or anionic groups to form a stable inner or primary sphere of attraction. Depending on the properties of the metal ion and the surrounding groups the primary sphere adopts some preferred geometry.*

2. *Outside the primary sphere there is a secondary sphere of attraction. In this secondary sphere there are usually present the requisite number of anions that satisfy the valence of the metal ion.*

3. *A metal ion has two kinds of valence : primary valence and secondary valence. The primary valence of the metal ion is satisfied by certain number of anions. The metal ion has still left on it some residual power of attraction for neutral groups of anions. The secondary valence leads to the formation of the primary sphere.*

We can take a look at $CoCl_3.\ 6NH_3$ from the viewpoint of Werner's coordination theory. Since the metal ion, coabalt (III), and the six NH_3 groups moved together in all the double decomposition reactions the compound was formulated as $[Co(NH_3)_6]Cl_3$. The first sphere has cobalt (III) and the six NH_3 groups tightly bound. The first sphere of attraction is written with a square bracket to indicate the strong interaction between the metal ion and the attached groups. The number of groups attached to cobalt (III) is six. The geometry in this particular case was proved by Werner to be octahedron. Outside the square bracket are present the three chloride groups to satisfy the primary valence of cobalt (III). Cobalt (III) thus has a primary valence of three and a secondary valence of six. Experiments with other similar compounds like $[Co(NH_3)_5(H_2O)]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_3Cl_3]$ revealed that anionic groups can simultaneously satisfy the primary and secondary valences of a metal ion. $[Pt(NH_3)_2Cl_2]$ has the primary valence of platinum (II) satisfied by the two chloride groups while the secondary valence is satisfied by the two NH_3 and the two Cl^- groups. In $[Cu(NH_3)_4]SO_4$ the primary valence of copper (II) is quenched by the binegative sulphate anion while the secondary valence is satisfied by the four NH_3 groups.

Some definitions used in coordination chemistry are given below :

1. The groups bound to the metal ion in the first sphere of attraction are called *ligands.*

2. The number of groups attached to the metal ion (or the number of stereochemical positions occupied by the attached ligands) is called the *coordination number.*

3. The entity composed of the metal ion and the ligands in the first sphere of attraction is known as a *complex.*

$[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5(H_2O)]^{3+}$, $[Co(NH_3)_3Cl_3]$, $[Cu(NH_3)_4]^{2+}$ and $[Pt(NH_3)_2Cl_2]$ are examples of complexes. The neutral groups NH_3, H_2O, and the anion Cl^- are examples of ligands. The coordination number of cobalt (III), copper (II) and platinum (II) are 6, 4 and 4 respectively. The respective geometries are octahedral and square planar.

From conductance measurements of the complex compounds in aqueous medium and from comparison with the standard values of different electrolytes Werner correctly determined the electrolytic character of the complexes. For example Werner reported the following data :

Complex and standard salts	Molar conductance ohms^{-1} cm^2 mole^{-1}	Electrolyte type
$[Co(NH_3)_6]Cl_3$	432	3 : 1
$[Co(en)_3]Cl_3$	352	3 : 1
$[Pt(NH_3)_2Cl_2]$ (*cis*)	5	non-electrolyte
$K_3[Fe(CN)_6]$	435	3 : 1
$CeCl_3$	408	3 : 1

en = $NH_2 - CH_2 - CH_2 - NH_2$ = ethylenediamine

6.2. DOUBLE SALTS

It has been customary for an elementary course on coordination chemistry in this country to learn the distinctions between a double salt and a complex salt. Before we go into this aspect we would like to introduce some examples of double salts. Under favourable circumstances two salts of two different metal ions may crystallise out of solution in the form of a double salt. Some double salts occur also in nature. Three important classes of double salts are cited below :

1. *Alums* : These are the double salts that crystallise from a 1 : 1 mixture of monovalent metal sulphates and trivalent metal sulphates. These are the alums with the general formula $M^{I}M^{III}(SO_4)_2.12H_2O$. The monovalent metal ions may be Na^+, K^+, Rb^+, Cs^+ or NH_4^+ while the trivalent ions may be Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+} etc. The common alum is $KAl(SO_4)_2.12H_2O$.

2. *Schonites* : These are the double salts that crystallise under favourable conditions from a 1 : 1 mixture of a monovalent metal sulphate and a bivalent metal sulphate. They may be represented by the formula $M^{I}_2M^{II}(SO_4)_2.6H_2O$. The most familiar example is Mohr's salt $(NH_4)_2Fe(SO_4)_2.6H_2O$.

3. *Carnallite type double chlorides* : These crystallise from an aqueous solution of 1 : 1 mixture of a monovalent chloride and a bivalent chloride. The best example is the naturally existing carnallite $KCl.MgCl_2.6H_2O$.

6.3. DOUBLE SALT AND COMPLEX SALT

At the very outset we would like to put on record that there is no real qualitative difference between a double salt and a complex salt. In aqueous solution our common alum dissociates into the component ions : Al^{3+}, K^+ and SO_4^{2-}. In aqueous medium the ions get aquated eg Al^{3+} forms $[Al(H_2O)_6]^{3+}$. It is argued that a double salt gives all the tests of the ions. It is true but then in aqueous medium whatever tests of the metal ions we perform they are the tests of the aquated metal ions. H_2O does function as a weak coordinating ligand. *A double salt is a weak complex salt. A stable complex salt does not dissociate in aqueous medium to give the aquo complex and hence many of the usual qualitative tests of the cation are not observed.* Some of the dissociations of some so-called double salts and complex salts are shown below :

$$\begin{aligned}
KAl(SO_4)_2.12H_2O &\rightleftharpoons K^+ + Al^{3+} + 2SO_4^{2-} + 12H_2O\\
Al^{3+} + 6H_2O &\rightarrow [Al(H_2O)_6]^{3+}\\
KCl.Mg\,Cl_2.6H_2O &\rightleftharpoons K^+ + Mg^{2+} + 3Cl^- + 6H_2O\\
Mg^{2+} + 6H_2O &\rightarrow [Mg(H_2O)_6]^{2+}\\
[Co(NH_3)_6]Cl_3 &\rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-\\
K_3[Cr(CN)_6] &\rightleftharpoons 3K^+ + [Cr(CN)_6]^{3-}\\
[Cu(NH_3)_4]SO_4 &\rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}
\end{aligned}$$

Aqueous solutions of potassium aluminium alum and potassium magnesium chloride are wholly dissociated into the component ions. Aluminium ion and magnesium ion are aquated readily. These aquo complexes readily respond to the usual tests of these ions. As against this $[Co(NH_3)_6]\ Cl_3$ and $K_3[Cr(CN)_6]$ dissociate to keep the complex entities intact. These entities are so very stable that the usual tests of chromium (III) or of cobalt (II) in aqueous medium are not positive.

6.4. PERFECT AND IMPERFECT COMPLEXES

Based on the nature of dissociation in aqueous medium complex compounds have been classified as (a) *perfect complexes* and (b) *imperfect complexes.* Perfect complexes are those which do not dissociate in aqueous medium to the metal ion and the (associated) ligands. Hence they cannot respond to the usual tests of the metal ions. Imperfect complexes are those which dissociate into the metal ion and the ligands. The metal ion then responds to the usual tests. In the examples cited in the earlier section $[Co(NH_3)_6]^{3+}$ and $[Cr(CN)_6]^{3-}$ are examples of perfect complexes while examples of imperfect complexes are provided by $[Ag(NH_3)_2]^+$ and $[Cd(CN)_4]^{2-}$. The last two break down in aqueous solution to respond to the usual tests of siver ion and cadmium ion. Silver can be precipitated as AgCl by the addition of HCl and CdS can be precipitated by passing H_2S through a solution of $[Cd(CN)_4]^{2-}$. The young reader should recall that the imperfect nature of the cadmicyanide complex has allowed us to develop a qualitative separation method for copper and cadmium in Group IIA of qualitative inorganic analysis.

6.5. COORDINATION NUMBER & GEOMETRY OF COMPLEXES

We have already mentioned in section 6.1 that the metal ion and the ligands jointly generate a suitable geometry. This geometry is primarily dependent on the coordination number but subtle variations are possible depending on the nature of the metal ion and the ligands. Although there is no hard and fast rule to decide which stereochemistry will result, we give a short resume of coordination number and geometry of complexes with suitable examples.

Table 6.1. Coordination number and geometrical shape

Coordination number	Geometrical shape	Examples
2	Linear	$[Ag(NH_3)_2]^+$ $(NH_2)HgCl$
3	Triangular planar	$[HgI_3]^-$
4	(a) Tetrahedral	$[CoCl_4]^{2-}$
	(b) Square planar	$[PtCl_4]^{2-}$ $[Ni(DMG)_2]^0$
6	Octahedral	$[Co(NH_3)_6]^{3+}$ $[Cr(CN)_6]^{3-}$

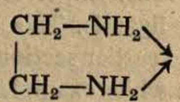
DMGH = dimethylglyoxime

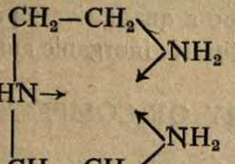
6.6. CLASSIFICATION OF LIGANDS

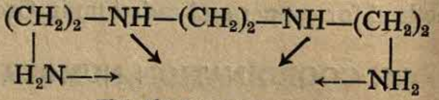
We are devoting this Chapter only to classical Werner complexes. The ligands that we have so far seen possess one common property : they all have one or more lone pairs of electrons on one of their atoms. It is the lone pair through which the ligand gets attached to the metal ion. X-ray crystal structures of many complexes show that the metal ion is linked to that atom of the ligand that carries the lone pair. Ligands can be classified according to the number of attachments offered to the metal ion. When the ligand has just *one lone pair of electrons* it can attach itself at just *one point*. It is capable of biting the metal ion at just one of the several permitted coordination points. Such a ligand is called *monodentate*.

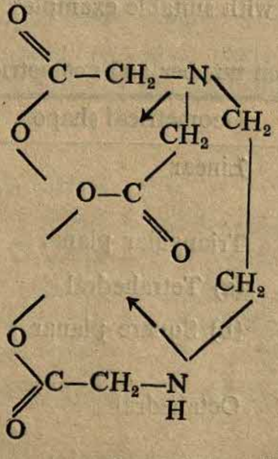
$\leftarrow NH_3$
Ammonia
(monodentate)

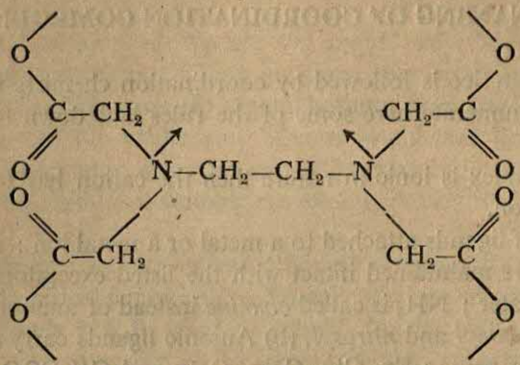
;


Ethylenediamine
(bidentate)


Diethylenetriamine
(tridentate)


Triethylene tetramine
(quadridentate)


Ethylenediamine triacetic acid anion (pentadentate)



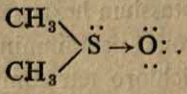
Ethylenediamine tetraacetic acid anion (sexadentate)

Fig. 6.2. Monodentate and polydentate ligands

When the ligand has two donor atoms (with lone pairs on) so disposed that it can go round the metal ion so as to bite it at two coordination points it is called a bidentate. Thus ethylenediamine (Fig 6.2), $NH_2-CH_2-CH_2-NH_2$, has two lone pairs on its two nitrogen atoms. It can attach itself at two coordination points of the metal ion to form a strain-free ring. Such a ligand is called a *bidentate*. If we proceed similarly we shall be able to find out many polydentate ligands : *bidentate, tridentate, quadridentate, pentadentate and sexadentate*. (Fig 6.2).

All polydentate ligands are known as chelating ligands. The word *chelate* means crab's claw. Chelating ligands impart extra stability to a metal complex because of added stability coming from the additional rings. Usually a 5-membered and a 6-membered ring are very stable while 4-membered and 7-membered rings are less stable.

It should be noted that the mere presence of two lone pairs will not make a ligand bidentate but that these lone pairs should be suitably placed so as to make a strain-free ring at the metal ion. Take for example the case of dimethyl sulphoxide.



$$(CH_3)_2\ddot{S} \rightarrow \ddot{O}:.$$

The sulphur atom is sp^2 hybridised ; two electrons in the two hybrid orbitals make sigma overlap with the two carbons while the third hybrid carrying a pair of electrons is donated to oxygen to make a coordinate covalent bond. Of the six electrons in the s^2p^4 outer orbitals two are retained in the third p-orbital which is outside the range of hybridisation. Thus we see that both oxygen and sulphur have lone pairs of electrons. But these cannot be attached simultaneously to one and the same metal ion as it will lead to a highly strained three-membered ring. This explains why dimethylsulphoxide never acts as a bidentate ligand. It acts as a monodentate ligand either through oxygen donor (to metal ions like Co^{2+}, Ni^{2+}, Zn^{2+} etc) or through sulphur donor (to metal ions Pd^{2+} and Pt^{2+}).

6.7. NAMING OF COORDINATION COMPOUNDS

Some standard parctice is followed by coordination chemists in the naming of complexes. We enumerate here some of the rules laid down for comparatively simpler cases.

1. If the complex is ionic in nature then the cation has to be named first and then the anion.

2. Naming of ligands attached to a metal or a metal ion : (a) Names of the neutral ligands are maintained intact with the listed exceptions : H_2O is called *aquo* instead of water ; NH_3 is called *ammine* instead of ammonia ; CO and NO are written as *carbonyl* and *nitrosyl*, (b) Anionic ligands carry a suffix *–o* at the end of their main name : F^-, Cl^-, CN^-, OH^- and CH_3COO^- are respectively known as *fluoro*, *chloro*, *cyano*, *hydroxo* and *acetato*, (c) Some polyatomic ligands may be attached to a metal ion through one or another donor centre. Depending on the donor atom attached naming is changed. Thus $\mathit{S}CN^-$ is called *thiocyanato* when attached through sulphur but *isothiocyanato* when attached through nitrogen ($\mathit{N}CS^-$). Similarly $\mathit{N}O_2^-$ is *nitro* when attached to a metal ion through nitrogen but *nitrito* when linked via oxygen ($\mathit{O}NO^-$).

3. Naming of mononuclear complexes : (a) If the complex is non-electrolytic or cationic then the anionic ligands are written first, then the neutral ligand and finally the cation. The oxidation state of the metal is included as Roman numeral within parenthesis. (b) In the case of an anionic complex entity a suffix *-ate* is added after the cation and then the oxidation state is mentioned. This rule is not always followed these days. (c) The number of the same ligand is expressed as a prefix *mono-*, *di-*, *tri-*, *tetra-*, *penta-* and *hexa-* etc. (d) In the case of geometrical isomers *cis* and *trans* are used at the beginning to indicate the nearest disposition or farthest disposition of the coordinated ligands.

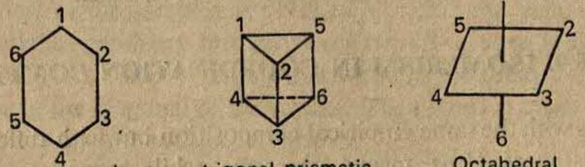
Given below are some typical examples :

1. $[Co(NH_3)_6]\ Cl_3$	Hexammine cobalt (III) chloride
2. $[Cr(H_2O)_6]\ Cl_3$	Hexaaquo chromium (III) chloride
3. $K_3[Cr(CN)_6]$	Potassium hexacyanochromiate (III)/chromium(III)
4. $[Co(NH_3)_5Br]\ SO_4$	Bromo pentammine cobalt (III) sulphate
5. $[Pt(NH_3)_4Cl_2]\ Br_2$	Dichloro tetrammine platinum (IV) bromide
6. $[Pt(NH_3)_2\ Cl_2]$	(*cis/trans*) dichloro diammine platinum (II)
7. $[Ni(CO)_4]$	Tetra carbonyl nickel (O)
8. $Na_3[Co(NO_2)_6]$	Sodium hexanitro cobaltiate (III)/cobalt (III)
9. $Na_2[Fe(CN)_5(NO)]$	Sodium pentacyano nitrosyl ferriate (II)/iron (II)
10. $K_4[Fe(CN)_6]$	Potassium hexacyano ferriate (II)/iron (II)

6.8. WERNER ESTABLISHES OCTAHEDRAL STEREOCHEMISTRY FOR SIX COORDINATE COMPLEXES

Werner did substantial amount of research on cobalt (III) and chromium (III) complexes. These two metal ions almost religiously follow a coordination number six. The question that agitated Werner was : what was the stereochemistry of these six-coordinate complexes. There are three geometries which can admit of this six-coordination. These are (a) planar hexagon (the one we see in benzene), (b) trigonal prism and (c) octahedron. Werner established that the octahedron was the preferred geometry. He used two techniques : (1) isomer counting and synthesis and (2) resolution of suitable complexes into optically active isomers.

6.8.1. Isomer counting : Isomer means different structural forms of compounds having the same empirical composition. We take the case of complex compounds of the general formula MA_4B_2 where M stands for the metal ion and A and B represent two monodentate ligands. A plane hexagon can produce three isomers related to the ortho (1, 2), meta (1, 3) and para (1, 4) derivatives of aromatic compounds. The trigonal prism also gives three isomers : (1, 2), (1, 3) and (1, 4). But the octahedron alone can give only two isomers: (1, 2) and (1, 6). Note that in an octahedron the (1, 2) isomer is the same as the (1, 3) or (1, 4) or the (1, 5) isomer. Similar is the case with complexes of empirical composition MA_3B_3. Werner prepared isomers of a large number of cobalt (III) and chromium (III) complexes of empirical composition MA_4B_2 and MA_3B_3. In no case could he isolate more than two isomers. Thus it was established that in six-coordinate complexes octahedron is the preferred stereochemistry.



	Hexagonal	trigonal prismatic	Octahedral
MA_4B_2	3 (1,2;1,3;1,4)	3 (1,2;1,3;1,4)	2 (1,2;1,6)
MA_3B_3	3 (1,2,3;1,2,4;1,3,5)	3 (1,2,3;1,2,5;1,2,6)	2 (1,2,3; 1,2,6)

Fig. 6.3. Number of possible isomers of MA_4B_2 and MA_3B_3 compounds on hexagonal, trigonal prismatic and octahedral models

6.8.2. Resolution of complexes. Optical activity in a compound appears when the compound can exist in two non-superimposable mirror image forms. We take the case of a tris (bidentate) metal complex like $[Co(en)_3]Cl_3$. (en = ethylenediamine = $NH_2 - CH_2 - CH_2 - NH_2$). It is found that in octahedral geometry alone there are possible two mirror images (Fig. 6.4) which are not superimposable. One mirror image cannot be made to superimpose the other by any rotation. This non-equivalence exists because the species do not possess planes or centres of symmetry. On the other hand the hexagon and the trigonal prism generate superimposable mirror images—this means that these latter mirror images do not have any separate identity. One of the two non-superimposable mirror images in the case of the octahedral $[Co(en)_3]^{3+}$ rotates the plane polarised light towards the right while the other does it to the left. The former isomer is known as dextrorotatory and the latter as the laevorotatory. Werner successfully resolved many tris (bidentate) cobalt (III)/chromium (III) complexes into their optical isomers. Thus the octahedral structure was established for six-coordinate metal complexes.

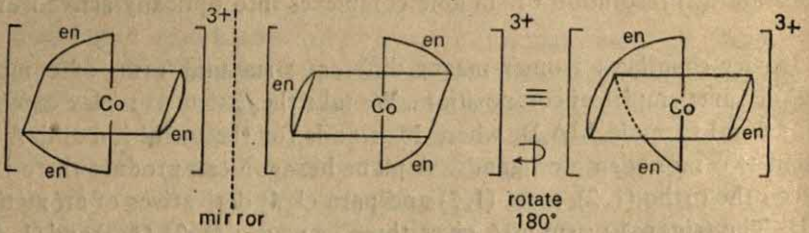


Fig. 6.4. Two optically active non-superimposable mirror images of tris (ethylenediamine) cobalt (III) cation

6.9. ISOMERISM IN COORDINATION COMPLEXES

Compounds with the same empirical composition but with different structures are known as isomers. '*Isos*' means '*the some*' while '*meros*' means '*the parts*'. In the arena of coordination complexes there are in fact a very large number of types of isomers. In this text we can talk about a selected few.

1. *Hydrate Isomerism* : The following three complexes of chromium (III) have different number of coordinated aquo ligands in the first sphere of attraction. The water molecules outside the coordination zone i.e. the first sphere can be absorbed by suitable dehydrating agents. Also addition of silver nitrate precipitates different amounts of chloride depending upon how many moles of chloride ion are outside the inner sphere.

$[Cr(H_2O)_6]Cl_3$; violet ; all three chlorides are precipitated.

$[CrCl(H_2O)_5]Cl_2.H_2O$: light green : two chlorides are precipitated.

$[CrCl_2(H_2O)_4]Cl\ 2H_2O$; green ; one chloride is precipitated.

Isomerism here arises due to different number of coordinated aquo molecules as also due to different number of coordinated chloride groups—which lead to the formation of differently charged complex ions. There is therefore a good case to designate the above three compounds as examples of ionisation isomers.

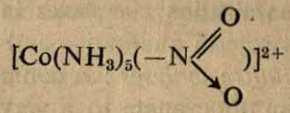
2. *Ionisation Isomerism* : This class of isomerism arises when different anions interchange their positions in the inner sphere and the outer sphere. In the first set of examples we see that bromide ion is a ligand while in the isomeric form it is not. In the latter case bromide remains as an anion outside the inner sphere.

$[Co(NH_3)_5\ Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$

$[Pt(NH_3)_4\ Br_2]Cl_2$ and $[Pt(NH_3)_4Cl_2]Br_2$

3. *Linkage Isomerism* : There are some polyatomic ligands which have two donor centres. Complex is named depending on which of the donor atoms is linked to the metal ion (see section 6.6).

$[Co(NH_3)_5(-O-NO)]^{2+}$ and



$[\mathrm{Co(NH_3)_5}(-\mathrm{N}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\langle}}\ )]^{2+}$

nitrito pentammine cobalt (III) nitro pentammine cobalt (III)

Similar isomerism may arise out of two ways of coordination of the $-SCN$ group. When the sulphur end is linked we call the isomer as the thiocyanato complex. When the nitrogen end is coordinated the complex is an isothiocyanato one.

4. *Geometrical Isomerism* : This type of isomerism arises when the isomers have the inner spheres of the same composition and geometry but different arrangement of the ligands within the same geometry. Simplest examples are provided by the two isomers of the complex $[Pt(NH_3)_2Cl_2]$. Both the isomers are known to possess square planar geometry but in one the two Cl^- groups (and automatically the two NH_3 groups) are next to each other while in the other they are opposite to each other along the diagonal of the square. The former is called the *cis* isomer whereas the latter is known as the *trans* isomer.

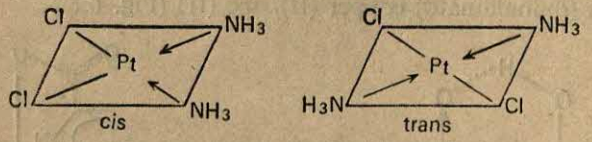


Fig. 6.5. Geometrical isomerism in dichloro diammine platinum (II)

5. *Optical Isomerism* : A consequence of geometrical isomerism in octahedral complexes is optical isomerism. Take the case of dichloro bis (ethylenediamine) cobalt (III). This complex can exist as the *trans* dichloro form and the *cis* dichloro form. The *cis* form can give rise to two non-superimposable mirror image forms. But the *trans* form, being symmetrical, cannot do so. One of the two distinct mirror image forms of the *cis* isomer will rotate the plane of polarised light to the right (*dextro-rotatory*) while the other rotates the plane of polarised light to the left (*laevorotatory*). We have mentioned in section 6.7.2 that tris (bidentate) metal complexes can also produce optical isomers.

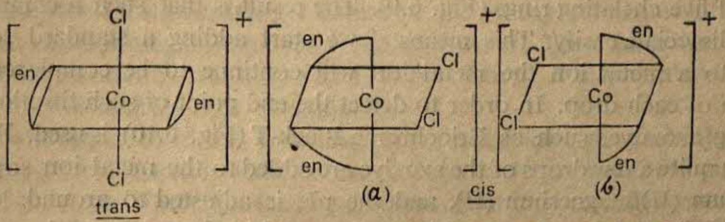


Fig. 6.6. *Trans* form and the two optically active *cis* forms of dichloro bis (ethylenediamine) cobalt (III)

6.10. USES OF COORDINATIN COMPLEXES IN ANALYSES AND IN INDUSTRY

6.10.1. Coordination complexes in inorganic analyses : Complexes have played significant role in qualitative and quantitave analyses of metal ions.

Qualitative analyses : A confirmatory test of iron (III) involves addition of ammonium thiocyanate to a very small amount of ferric ion. A blood red colouration appears immediately due to the formation of $[Fe(NCS)_6]^{3-}$, $[Fe(NCS)(H_2O)_5]^{2+}$ type complexes. Cobalt (II) can be detected by the addition of HCl to the very pale pink coloured $[Co(H_2O)_6]^{2+}$ when the deep blue coloured $[CoCl_4]^{2-}$ (tetrahedral) complex is formed. Very small amount of nickel (II) can be detected by adding little dimethylgloxime in neutral or slightly ammoniacal solution. A very attractive rose-red coloured bis (dimethylglyoximato) nickel (II) is precipitated.

Quantitative analysis : There are some chelating organic ligands which react with certain metal ions under specified pH conditions to give quantitative precipitates of the metal complexes in non-electrolytic forms. One fine example is bis (dimethylglyoximato) nickel (II). The precipitate can be filtered, washed, dried and finally weighed to ascertain the quantity of nickel present in the given sample (Fig. 6.7). Quinaldinic acid precipitates copper (II) and zinc (II) quantitatively as bis (quinaldinato) copper (II)/zinc (II) (Fig. 6.8.).

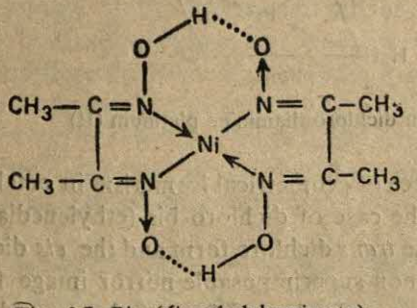


Fig. 6.7. Bis (dimethylglyoximato) nickel (II)

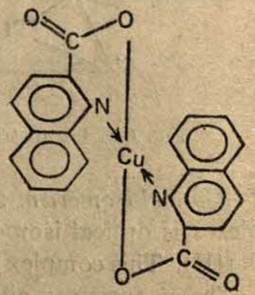


Fig. 6.8. Bis (quinaldinato) copper (II)

Complexometric titration of metal ions : Ethylenediamine tetraacetic acid (Fig. 6.2) is a powerful sexadentate ligand. It can hold a metal ion tightly by means of five chelating rings (Fig. 6.9). The result is that such a complexed ion cannot dissociate easily. This means if we start adding a standard solution of EDTA to a metal ion the metal ion will continue to be complexed with the addition of each drop. In order to detect the end point of such titration a weak chelating azo dye, such as Eriochrome Black-T (Fig. 6.10), is used. Prior to the titration quite a few drops of the azo dye are added to the metal ion solution, say of calcium (II)/magnesium (II), and the pH is adjusted to around 10-11. The colour of the azo dye alone at this pH is *blue* while the colour of the calcium (II)/magnesium (II)—azo dye complex is red-violet. As we add the standard solution of EDTA to this solution each drop of EDTA forms a strong colourless calcium (II)/magnesium (II) complex of EDTA. As the last few drops of EDTA are added the chelated azo-dye is released from complexation and there is a colour change from *red-violet* to *blue*. Since such titrations involve complex formation these are known as *complexometric/chelatometric/chelometric* titration. This is the basis of modern method of determination of hardness of water.

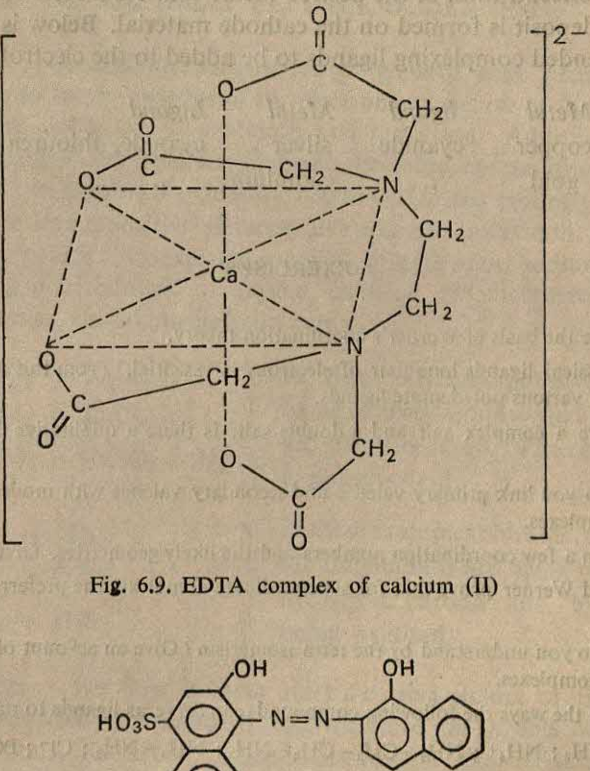


Fig. 6.9. EDTA complex of calcium (II)

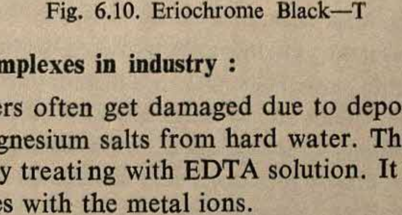


Fig. 6.10. Eriochrome Black—T

6.9.2. Coordination complexes in industry :

1. Industrial boilers often get damaged due to deposit of insoluble $CaCO_3$, and other calcium/magnesium salts from hard water. These undesirable deposits can be dissolved out by treating with EDTA solution. It follows that EDTA will form soluble complexes with the metal ions.

2. Purification of nickel, free from other metal ions, particularly cobalt has been achieved via reaction with carbon monoxide. At around 50°C nickel reacts with CO to form $Ni(CO)_4$. But under this condition no other metal forms a carbonyl. $Ni(CO)_4$ is then decomposed at about 200°C to get very pure form of nickel.

3. Electroplating is a very useful and important industrial process. The article to be electroplated is cleaned and then suspended at the cathode. The choice of the electrolyte is of utmost importance. Using an aqueous solution of the metal ion to be electrodeposited usually gives a coarse and incoherent deposit. This could be checked by using a complexing agent in the electrolyte. Under this condition a stable complex is formed, which dissociates only to a small extent to give a low concentration of the desired metal ion. As a result a slow and very coherent, fine deposit is formed on the cathode material. Below is given a list of some recommended complexing ligands to be added to the electrolytic bath.

Metal	*ligand*	*Metal*	*Ligand*
copper	cyanide	silver	cyanide, thiourea
gold	,,	cadmium	,,

EXERCISES

1. Describe the basis of Werner's coordination theory.

2. For classical ligands lone pair of electrons is essential. From this standpoint present a classification of various polydentate ligands.

3. Compare a complex salt and a double salt. Is there a qualitative difference between the two ?

4. How do you link primary valence and secondary valence with modern terminology of coordination complexes.

5. Mention a few coordination numbers and the likely geometries. Give examples.

6. How did Werner prove that for six coordinate complexes the preferred geometry is an octahedron ?

7. What do you understand by the term isomerism? Give an account of isomerism found in coordination complexes.

8. Discuss the ways the following compounds can serve as ligands to metal ions :

CH_4, NH_3 ; NH_4^+ ; $NH_2-CH_2-CH_2-NH_2$; NH_2-NH_2 ; Cl^- ; PCl_3

9. Write down the names of the following complexes :

(*a*) $[Ni(H_2O)_6]Cl_3$ (*b*) $[Pt(NH_3)_2Cl_2]$ (*c*) $[PtCl_4]^{2-}$ (*d*) $[Co(NH_3)_3Cl_3]$

10. Give an account of the applications of coordination complexes in qualitative analysis and in industry.

CHAPTER 7

OXIDATION-REDUCTION REACTIONS

7.1. NEWER IDEAS REPLACE OLDER ONES

7.1.1. Older Ideas : Oxidation-reduction reactions have been recognised since a long time. Prior to our knowledge of the electronic structure of matter we used to use the classical definition of oxidation and reduction. Addition of oxygen or other electronegative elements like chlorine, bromine, etc. to some element or compound used to indicate an oxidation reaction. On the contrary addition of hydrogen or other electropositive elements like sodium, potassium, etc. used to mean a reduction process. Conversely removal of hydrogen, sodium, etc stood for oxidation. Again withdrawal of oxygen, chlorine, etc. meant reduction. We can take, for instance, the following reactions :

1. $2K + \frac{1}{2}O_2 \rightarrow K_2O$ 2. $Zn + Cl_2 \rightarrow ZnCl_2$ 3. $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$	In these instances potassium, zinc are being oxidised while oxygen and chlorine are being reduced. The case of H_2SO_4 is not clear-cut.
4. $Cl_2 + H_2 \rightarrow 2HCl$ 5. $CO_2 + C \rightarrow 2CO$ 6. $S + H_2 \rightarrow H_2S$	In these examples chlorine, carbon dioxide and sulphur are being reduced while hydrogen, carbon and hydrogen are being oxidised.

7.1.2. Newer Ideas : We now possess quite a correct picture of the electronic structure of matter. The extranuclear electrons are the agents which initiate chemical interactions. Therefore a generalisation of the oxidation-reduction processes must be sought in the transfer of electrons from one reactant to another. It is now universally acclaimed that transfer of electrons from one substance to another makes one substance positively charged while the other substance gets negatively charged. *Loss of electrons means oxidation while gain of electrons means reduction. Since in all chemical reactions electrons are conserved, oxidation-reduction reactions must proceed simultaneously. The substance that forces reduction i.e supplies electrons is called the reducing agent or the reductant.* On the other hand *the substance which forces oxidation i.e. takes up the electrons is known as oxidising agent or the oxidant.* The electronic definition is a generalised definition because we are defining the system in terms of a fundamental particle, namely the electron. The classical definition involved some chosen elements whose removal or addition led to the oxidation-reduction processes.

In the first example the element potassium is a member of the group IA and hence has a single valence electron. This single valence electron is lost to an oxygen atom. Two such electrons coming from two potassium atoms move into the oxygen atom to make it a dinegative oxide ion. Thus we say potassium is oxidised while oxygen is reduced. In the process of such electron transfer both the potassium ion and the oxide ion attain the stable electronic configuration of the nearest noble gases.

$$\begin{array}{l} 2[K \rightarrow K^+ + e] \\ \frac{1}{2}O_2 + 2e \rightarrow O_2^- \\ \hline 2K + \frac{1}{2}O_2 \rightarrow K_2^+\, O^{2-} \end{array}$$

$$\begin{array}{lll} K & : & 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^1 \\ & & \qquad \downarrow -e \\ K^+ & : & 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6 \text{ [Ar configuration]} \\ O & : & 1s^2\, 2s^2\, 2p^4 \\ & & \qquad \downarrow + 2e \\ O^{2-} & : & 1s^2\, 2s^2\, 2p^6 \text{ [Ne configuration]} \end{array}$$

Taking the case of Zn/H_2SO_4 reaction we see that zinc atom releases two valence electrons to the two H^+ ions. In the process a dipositive zinc ion and a neutral molecule of hydrogen is formed.

$$Zn \rightarrow Zn^{2+} + 2e \quad ; \quad H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

$$2H^+ + 2e \rightarrow H_2 \quad ;$$

7.1.3. Limitation of the Classical View : It is an experimental fact that the alkalies and the alkaline earths react with hydrogen to form hydrides. For example, lithium and hydrogen give LiH. Classical definition would tell us that lithium is reduced by hydrogen i.e hydrogen acts as the reducing agent. Electrolysis of fused LiH gives lithium at the cathode while hydrogen is liberated at the anode. This means lithium is positively charged while hydrogen is negatively charged. This is possible only if lithium atom transfers its valence electron to hydrogen i.e. hydrogen acts in this particular case as an oxidising agent.

$$LiH \rightarrow Li^+ + H^-$$

at the cathode : $Li^+ + e \rightarrow Li$

at the anode : $2H^- \rightarrow H_2 + 2e$

reaction between lithium and hydrogen

$$\begin{array}{l} Li \rightarrow Li^+ + e \\ H + e \rightarrow H^- \\ \hline Li + H \rightarrow LiH \end{array}$$

7.1.4. Limitation of the Electronic View : The electronic definition given above assumes electron transfer. Electron transfer from one substance to another may take place only if the reactants lead to the formation of an ionic compound like NaCl, K_2O etc. Obviously it is difficult to extend the idea to covalent compound where electrons are not transferred but shared. We therefore find it difficult to cover CO_2, HCl, H_2S etc. under this scheme. The concept of *oxidation number* has been introduced for this purpose. *Oxidation number is defined as the atomic number of the atom minus the number of the electrons remaining in the different orbitals.* More simply, *oxidation number is the effective charge on the atom.* Oxidation number and oxidation state are used to convey the same meaning. The concept appears straightforward for ionic compounds like NaCl. In NaCl the charge on sodium is + 1 while that on chlorine is −1. The question that confronts us is how do we know the net charges on the different atoms in

CO_2, H_2O, etc. Evaluation of the net charge on each atom would require an exact knowledge of the charge distribution throughout the molecules. This is not a simple affair. Chemists have therefore developed an ingenious, arbitrary method to solve this problem. *Oxidation state or oxidation number is a fictitious number assigned to an atom in a molecule assuming that all the bonds in the molecule are ionic in nature.*

7.2. OXIDATION NUMBER AND ALTERNATIVE EXPLANATION OF OXIDATION-REDUCTION

Oxidation numbers of the ions in an ionic compound can be ascertained easily. The number of electrons which are withdrawn from or put into a neutral atom is the oxidation number of the particular ion of an ionic compound. Since sodium loses one electron while chlorine gains one electron the oxidation numbers of sodium and chloride ions are respectively $+1$ and -1 respectively. However assignment of oxidation number in respect of covalent compounds requires some arbitrary rules.

1. Oxidation number of all elements in elementary state is zero.

2. The algebraic sum of the oxidation numbers of all the atoms in a compound is also zero. (This has to be the case as the molecule as a whole is neutral.)

3. The oxidation number of oxygen is taken as -2. Exceptions to this are found in the compounds H_2O_2 and F_2O. In H_2O_2 oxygen is assigned an oxidation number -1 as hydrogen is given a value $+1$. We have to appreciate that oxygen being more electronegative has to have a negative value and that the algebraic sum of all the oxidation numbers taken together must be zero. Similar will be the case with alkali and alkaline earth peroxides. In F_2O we must bear it in mind that oxygen is less electronegative than fluorine. So each fluorine is assigned -1 so that oxygen in F_2O has an oxidation number $+2$.

4. Hydrogen usually is assigened an oxidation number of $+1$ but in alkali metal/alkaline earth hydrides it is given a value of -1. The explanation obviously is higher electronegativity of hydrogen.

We utilise the above stated rules to develop Table 7.1

Table 7.1. Oxidation Numbers of Various Elements in Compounds

Compounds	Oxidation Numbers
CH_4	$C = -4$; $H = +1$
H_2O	$O = -2$; $H = +1$
NaH	$Na = +1$; $H = -1$
$CHCl_3$	$C = +2$; $H = +1$; $Cl = -1$
$K_2Cr_2O_7$	$K = +1$; $Cr = +6$; $O = -2$
$KMnO_4$	$K = +1$; $Mn = +7$; $O = -2$
$Na_2S_2O_3$	$Na = +1$; $S = +2$; $O = -2$

The more positive the oxidation number is the greater is the loss of electron density. Therefore *a change towards higher oxidation number means an oxidation.* On the other hand lowering of oxidation number means feeding of more of electron density. *A change towards lower oxidation number means reduction.* A reaction cannot be considered as oxidation-reduction reaction unless there occur a simultaneous increase and decrease in oxidation numbers in the reactants and the products.

The following reactions are oxidation-reduction reactions because there are changes in the oxidation numbers. For example in the first reaction oxidation

$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$$
$$Zn + H_2SO_4 \rightarrow Zn\,SO_4 + H_2$$

number of mercury changes from 2 to 1 while that of tin changes from 2 to 4. So mercury (II) is reduced to mercury (I) while tin (II) is oxidised to tin (IV). In the second instance oxidation number of zinc changes from 0 to 2 whereas that of hydrogen gets reduced from 1 to 0.

An atom (i.e. an element) is oxidised when its oxidation number increases. On the contrary *an atom (i.e. an element) is reduced when its oxidation number decreases.*

The following reaction cannot be considered as oxidation-reduction since there is no change in oxidation number of any of the atoms. The oxidation numbers

$$2K_2CrO_4 + 2HCl \rightarrow K_2Cr_2O_7 + 2KCl + H_2O$$

of potassium, chromium, oxygen, hydrogen and chlorine remain the same.

A substance is termed an oxidant if it succeeds in increasing the oxidation number of an element. A reductant lowers the oxidation number of an element. In the above examples $SnCl_2$ and Zn are the reducing agents whereas $HgCl_2$ and H^+ are the oxidising agents.

7.3. BALANCING OXIDAION-REDUCTION REACTIONS BY ION-ELECTRON METHOD

Oxidation-reduction reactions can be profitably balanced by handling the oxidising and the reducing ions and the number of electrons involved in the process. Such an exercise requires the following rules to be observed in a disciplined way :

1. Oxidation half reaction and the reduction half reactions are to be written out.
2. In the half reactions mass balance and electron balance have to be made.
3. The half reactions have to be multiplied with appropriate numbers so that same number of electrons participate in both the half reactions.
4. The two half reactions, as balanced above, have to be added so as to get the total reaction.

We now take several representative examples to illustrate the balancing procedure.

Problem 1 : Electrolysis of anhydrous ferric chloride gives iron at the cathode and chlorine at the anode. Write the oxidation-reduction reaction by the ion-electron method.

Reduction half-reaction : $Fe^{3+} + 3e \rightarrow Fe$
Oxidation half-reaction : $2Cl^- \rightarrow Cl_2 + 2e$

In order to make mass balance and electron balance the reduction half-reaction is multiplied by 2 and the oxidation half-reaction by 3. Addition of the two half-reactions gives the full reaction.

$$\begin{array}{rcl} 2Fe^{3+} + 6e & \rightarrow & 2Fe \\ 6Cl^- & \rightarrow & 3Cl_2 + 6e \\ \hline 2Fe^{3+} + 6Cl^- & \rightarrow & 2Fe + 3Cl_2 \end{array}$$

Problem 2 : In acidic medium permanganate ion reacts with ferrous salts to give ferric salt and manganous salt. Write the total reaction.

Reduction half-reaction : $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$
Oxidation half-reaction : $Fe^{2+} \rightarrow Fe^{3+} + e$

It is obvious that in order to make electron balance the reduction half-reaction is to be multiplied by 1 and the oxidation reaction by 5. Addition of the half-reactions gives the final reaction.

$$\begin{array}{rcl} MnO_4^- + 8H^+ + 5e & \rightarrow & Mn^{2+} + 4H_2O \\ 5Fe^{2+} & \rightarrow & 5Fe^{3+} + 5e \\ \hline MnO_4^- + 5Fe^{2+} + 8H^+ & \rightarrow & Mn^{2+} + 5Fe^{3+} + 4H_2O \end{array}$$

Problem 3 : Permanganate reacts with hydrochloric acid to produce manganous salt and chlorine. Write the balanced ionic equation.

Reduction half-reaction : $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$
Oxidation half-reaction : $2Cl^- \rightarrow Cl_2 + 2e$

We have to multiply the reduction half-reaction by 2 and the oxidation half-reaction by 5. Given below is the full reaction :

$$\begin{array}{rcl} 2MnO_4^- + 16H^+ + 10e & \rightarrow & 2Mn^{2+} + 8H_2O \\ 10Cl^- & \rightarrow & 5Cl_2 + 10e \\ \hline 2MnO_4^- + 16H^+ + 10Cl^- & \rightarrow & 2Mn^{2+} + 5Cl_2 + 8H_2O \end{array}$$

Problem 4 : Potassium dichromate reacts with potassium iodide in presence of acid to form chromium (III) and liberate iodine.

Reduction half-reaction : $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$
Oxidation half-reaction : $2I^- \rightarrow I_2 + 2e$

We multiply the reduction half-reaction by 2 and the oxidation half-reaction by 6. Thereafter addition has to be done.

$$\begin{array}{rcl} 2Cr_2O_7^{2-} + 28H^+ + 12e & \rightarrow & 4Cr^{3+} + 14H_2O \\ 12I^- & \rightarrow & 6I_2 + 12e \\ \hline 2Cr_2O_7^{2-} + 28H^+ + 12I^- & \rightarrow & 4Cr^{3+} + 6I_2 + 14H_2O \end{array}$$

i.e. $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

Problem 5 : Sodium thiosulphate and iodine react to produce tetrathionate and sodium iodide. Write the balanced ionic equation.

Reduction half-reaction : $I_2 + 2e \rightarrow 2I^-$

Oxidation half-reaction : $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e$

Since both the reactions involve the same number of electrons *i.e.* 2 we merely have to add the two reactions to get the full reaction.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Problem 6 : On the addition of potassium iodide to a solution of copper (II) sulphate iodine is liberated and a precipitate of cuprous iodide separates. Write the ionic equation.

Reduction half-reaction : $Cu^{2+} + e \rightarrow Cu^+$

Oxidation half-reaction : $2I^- \rightarrow I_2 + 2e$

The reduction half-reaction is to be multiplied by 2 and the other counterpart by 1. Addition provides the full reaction.

$$\begin{array}{r} 2Cu^{2+} + 2e \rightarrow 2Cu^+ \\ 2I^- \rightarrow I_2 + 2e \\ \hline 2Cu^{2+} + 2I^- \rightarrow 2Cu^+ + I_2 \end{array}$$

7.4. BALANCING OF OXIDATION-REDUCTION REACTIONS BY OXIDATION NUMBER METHOD

In the ion-electron method we concentrated upon equating the number of electrons on both the reductant and oxidant sides. Here we have to concentrate on the oxidation numbers.

1. Locate the atoms or ions whose oxidation numbers are changing. Write the equations indicating the decrease in the oxidation number and the increase in the oxidation number.
2. Multiply the two equations by appropriate numbers so that the decrease in the oxidation number equals the increase.
3. Now make atom balance by taking required number of H^+ or OH^- ions depending on whether the operating medium is acidic or alkaline.

Problem 1 : Electrolysis of anhydrous ferric chloride gives iron at the cathode and chlorine at the anode.

Reduction : $Fe^{3+} \rightarrow Fe$: Decrease in oxidation number = 3

Oxidation : $2Cl^- \rightarrow Cl_2$: Increase in oxidation number = 2

In order to strike a balance between the decrease and increase in oxidation numbers of the oxidant and the reductant the reduction reaction has to be multiplied by 2 and the oxidation reaction by 3. No problem arises with atom balance. Addition then gives us the final result.

$$\begin{array}{rcl} 2Fe^{3+} & \rightarrow & 2Fe \\ 6Cl^- & \rightarrow & 3Cl_2 \\ \hline 2Fe^{3+} + 6Cl^- & \rightarrow & 2Fe + 3Cl_2 \end{array}$$

Problem 2 : In acidic medium permanganate oxidises ferrous to ferric and itself gets reduced to manganous ion.

Reduction : $MnO_4^- \rightarrow Mn^{2+}$; Decrease in oxidation number = 5
Oxidation : $Fe^{2+} \rightarrow Fe^{3+}$; Increase in oxidation number = 1

The reduction reaction is to be multiplied by 1 and the oxidation reaction by 5. In order to achieve atom balance of the four oxygen atoms we have to bring in $8H^+$ from the acidic solution. Addition of the two reactions will provide the balanced equation.

$$\begin{array}{rcl} MnO_4^- + 8H^+ & \rightarrow & Mn^{2+} + 4H_2O \\ 5Fe^{2+} & \rightarrow & 5Fe^{3+} \\ \hline MnO_4^- + 5Fe^{2+} + 8H^+ & \rightarrow & Mn^{2+} + 5Fe^{3+} + 4H_2O \end{array}$$

Problem 3 : Permanganate reacts with HCl to give chlorine while producing manganous salt.

Reduction : $MnO_4^- \rightarrow Mn^{2+}$; Decrease in oxidation number = 5
Oxidation : $2Cl^- \rightarrow Cl_2$; Increase in oxidation number = 2

Cross multiplication of the two reactions by 2 and 5 and bringing in $16H^+$ ions from the acidic medium to effect balance of the 8 oxygen atoms will produce the final balanced reaction.

$$2MnO_4^- \rightarrow 2Mn^{2+} \; ; \; 10Cl^- \rightarrow 5Cl_2$$

$$\therefore \quad 2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$$

Problem 4. Potassium dichromate reacts with potassium iodide in presence of acid to liberate iodine along with the formation of chromium (III).

Reduction : $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$; Decrease in oxidation number = 6
Oxidation : $I^- \rightarrow I$; Increase in oxidation number = 1

The two processes have to be cross multiplied by 1 and 6. Besides, for each dichromate atom balance would require adding $14H^+$ ions. Thus the final reaction will take the following form :

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

Problem 5. Potassium dichromate and ferrous sulphate react in presence of acid to form ferric ion and chromic ion.

Reduction : $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$; Decrease in oxidation number = 6
Oxidation : $Fe^{2+} \rightarrow Fe^{3+}$; Increase in oxidation number = 1

Now cross multiplication will involve 1 and 6 for the reduction and the oxidation process respectively. Moreover to account for the mass balance of the seven oxygen atoms we have to use $14H^+$ ions from the acid medium.

$$Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+}$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Problem 6 : Potassium permanganate and manganese dioxide react in KOH medium to form potassium manganate and water.

Reduction : $MnO_4^- \rightarrow MnO_4^{2-}$; Decrease in oxidation number = 1
Oxidation : $MnO_2 \rightarrow MnO_4^{2-}$; Increase in oxidation number = 2

So the reduction process has to be multiplied by 2 and the oxidation process by 1.

$$2MnO_4^- \rightarrow 2MnO_4^{2-}$$

$$\underline{MnO_2 \rightarrow MnO_4^{2-}}$$

$$2MnO_4^- + MnO_2 \rightarrow 3MnO_4^{2-}$$

To make atom balance of the oxygen atoms we have to use 4 OH^- ions on the left hand side. The full reaction is as given below :

$$2MnO_4^- + MnO_2 + 4OH^- \rightarrow 3MnO_4^{2-} + 2H_2O$$

7.5. TRANSFORMATION OF CHEMICAL ENERGY TO ELECTRICAL ENERGY : THE STORY OF ELECTROCHEMICAL CELL

We have observed so far that the basis of oxidation-reduction reactions is transfer of electrons. In ordinary cases the two reactions cannot be separated and hence the flow of electrons from one partner to another is not normally observed. For instance if we dip a zinc rod into a solution of copper (II) sulphate we will be able to make some interesting observations. The solution gets warm, the colour of the copper (II) solution fades, there is a deposition of metallic copper onto the surface of zinc rod and finally on testing the solution we do find that zinc (II) ions have moved into the solution. All these facts find a ready explanation in the following oxidation-reduction reactions :

Oxidation : $Zn \rightarrow Zn^{2+} + 2e$
Reduction : $Cu^{2+} + 2e \rightarrow Cu$

Once we push in the zinc rod into the copper (II) solution the above two reactions start occurring simultaneously. We therefore do not observe the flow of electrons from the zinc rod to the copper (II) solution leading to the deposition of the metallic copper onto the surface of the zinc rod. But the separation of the above two reactions and the flow of electrons have actually been observed in the Daniell cell.

7.5.1. The Daniell Cell : The cell consists of a rectangular vessel with a porous partition in the middle. On one side of the partition a zinc plate is immersed into a solution of zinc (II) while on the other side of the partition a copper plate hangs into a solution of copper (II) (Fig. 7.1). The zinc plate and the copper plate are connected to an ammeter. To our great satisfaction we find that a current flows. This is possible because there is flow of electrons from zinc plate through the external circuit. The ammeter connection does indicate that electrons are coming from the zinc plate. This is possible only if metallic zinc undergoes oxidation producing zinc (II) ions and electrons. The zinc (II) ions pass into the solution while the electrons move up the connecting wire into the ammeter. Accumulation of positively charged zinc (II) ions takes place in the zinc plate compartment. As the electrons travel through the ammeter and arrive at the copper plate copper (II) ions are reduced and are deposited on the copper plate. As a consequence there is depletion of positive ions and accumulation of negative sulphate ions in the copper plate copartment. The purpose of the porous barrier is to hinder free mixing of the two solutions but to allow the necessary movement of charged ions from one compartment to the other so that there is no excessive charge accumulation in either compartment. The Daniell cell may also be constructed by using two separate beakers to hold the two separate solutions and the plates and then joining them by a salt bridge *i.e.* a tube filled with a gelatinous material containing NH_4NO_3 or KCl electrolyte. Yet another approach is to place a porous pot inside a wider beaker. One solution is taken in the beaker while the other in the porous pot.

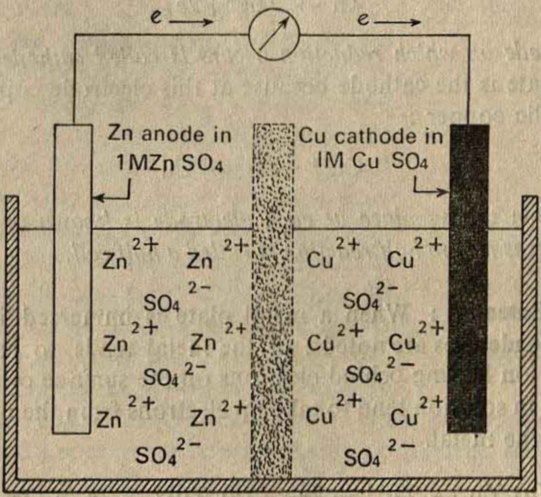


Fig. 7.1. The Daniell cell—an example of an electrochemical cell

Daniell cell is an example of an *electrochemical cell,* also known as *voltaic cell* or *galvanic cell. An electrochemical cell is an arrangement of chemicals so as to produce electrical energy at the expense of chemical energy originating from* *spontaneous oxidation-reduction reaction.* The following points should be remembered :

1. *A conducting surface on which some reaction involving electrons takes place is called an electrode.*

2. *The electrode on which oxidation occurs is called anode.* In the Daniell cell the zinc plate is the anode as metallic zinc is oxidised to zinc (II) :

$$Zn \rightarrow Zn^{2+} + 2e$$

3. *The electrode on which reduction occurs is called cathode.* In the Daniell cell the copper plate is the cathode because at this electrode copper (II) ions are reduced to metallic copper :

$$Cu^{2+} + 2e \rightarrow Cu$$

4. *The reaction taking place at each electrode is known as a half reaction. The system that gives rise to half reaction is called a half cell.*

7.5.2. Electrode Potential : When a metal plate is immersed in a solution of its own ions two tendencies are noted : (*a*) the metal tends to pass into solution as positive metal ion leaving behind electrons on the surface of the metal plate ; (*b*) the metal ions in solution tend to take up electrons from the metal surface and get converted to the metal.

$$(a)\ Zn \rightarrow Zn^{2+} + 2e\ ;\quad (b)\ Zn^{2+} + 2e \rightarrow Zn$$

Which of these two opposite trends is more important is decided by the electron releasing capacity of the metal ion. A double layer is set up at the immediate vicinity of the metal electrode. Under such situation the metal plate and the solution of its own ions develop a potential. The potential developed by a half cell is called a half-cell potential or *single electrode potential.* Combining together of two half-cells generate a complete cell which has a characteristic potential called *cell potential.* The cell potential is a function of concentration of the ions in the two half cells. In the case of the Daniell cell at equal concentrations of the zinc (II) and copper (II) ions a potentiometer records a potential difference *i.e.* voltage of 1.1 volts. Different combinations of half-cells produce different voltages.

7.5.3. Single Electrode Potential : *Single electrode potential is defined as the potential developed by a half-cell composed of a metal immersed in a solution of its salt under standard states.* The standard states refer to 1 M concentration for the dissolved salts, 1-atmosphere pressure for all gases. But then it is not possible to measure the half cell potential directly because a potentiometer can record the voltage or potential difference of a full cell. Therefore a half-cell has to be combined with another half-cell whose potential is known. Chemists have set hydrogen gas-hydrogen ion in contact with an inert electrode like platinised platinum as the *reference half-cell.* The reactants and the products of the half-cell

$$2H^+(aq) + 2e \rightarrow H_2(g)$$

are in their standard states. The half-cell potential of this reference is taken as zero volts. A platinised platinum electrode is suspended into a solution of 1MH^+ ion (usually H_2SO_4) and hydrogen gas is then led through at 1 atmosphere pressure (Fig. 7.2). The platinum wire acts as the conducting medium and assists in establishing equilibrium between H^+ ion and H_2 molecules. When this reference electrode is connected to another metal ion/metal half-cell through a potentiometer the voltage recorded will be the standard electrode potential of the metal ion-metal half-cell. During all these measurements the metal ion is maintained under standard state *i.e.* 1 *M* or more correctly at *unit activity*. We now look into the sign convention of these standard electrode potentials. Let us take the case of the Mg^{2+}/Mg coupled with the hydrogen electrode. When we go for measurement of the voltage *i.e.* the *electromotive force* (e.m.f.) of this cell we note that proper electrical connection is made only when the magnesium end is joined to the negative end of the potentiomer. This gives us a clue that the magnesium end of the cell is the negative end *i.e.* excess electrons are being released at the surface of the

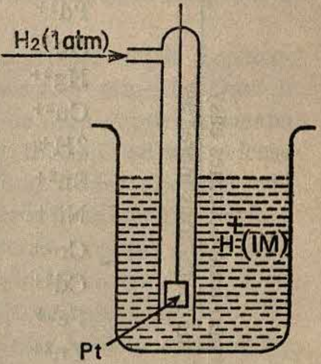


Fig. 7.2. Hydrogen electrode

Mg – $MgSO_4$ solution | (Pt)H_2 – H_2SO_4 solution
$^aMg^{2+} = 1$ | $^aH^+ = 1$
(–) Potentiometer (+) ; $E° = -2.37$ volts

magnesium metal. According to the *international convention* the standard electrode potential of the Mg^{2+}/Mg electrode is to be represented with a negative sign *i.e.* as *standard reduction potential.* Similar negative potential of –0.763 volts is

$$Zn^{2+} + 2e \rightleftharpoons Zn \ ; \ E° = -0.763 \text{ volts}$$

recorded for the Zn^{2+}/Zn half-cell. As against these cases if we examine the Cu^{2+}/Cu coupled with the hydrogen electrode we will see that this time the hydrogen end has to be connected to the negative end and the copper to the positive end of the potentiometer. This indicates that the tendency of copper metal to release electrons is much less than that of hydrogen. According to international convention

Cu – $CuSO_4$ solution | (Pt)H_2–H_2SO_4 solution
$^aCu^{2+} = 1$ | $^aH^+ = 1$
(+)Potentiometer(–) ; $E° = +0.337$ volts

the standard electrode potential of Cu^{2+}/Cu is expressed with a positive sign ($E° = +\ 0.337$ volts). Table 7.2 records some standard reduction potentials.

Table 7.2. Standard Electrode (Reduction) Potentials at 25°C

↑ Reduction of the metal ions becomes easy

↑ Oxidising ability of the metal ions increases

Half-reaction	Reduction Potential
$Pt^{2+} + 2e \rightleftharpoons Pt$	+ 1.200 volts
$Pd^{2+} + 2e \rightleftharpoons Pd$	+ 0.987
$Ag^{+} + e \rightleftharpoons Ag$	+ 0.799
$Hg^{2+} + 2e \rightleftharpoons Hg$	+ 0.789
$Cu^{2+} + 2e \rightleftharpoons Cu$	+ 0.337
$2H^{+} + 2e \rightleftharpoons H_2$	+ 0.000
$Sn^{2+} + 2e \rightleftharpoons Sn$	− 0.136
$Ni^{2+} + 2e \rightleftharpoons Ni$	− 0.250
$Co^{2+} + 2e \rightleftharpoons Co$	− 0.277
$Cd^{2+} + 2e \rightleftharpoons Cd$	− 0.403
$Fe^{2+} + 2e \rightleftharpoons Fe$	− 0.440
$Zn^{2+} + 2e \rightleftharpoons Zn$	− 0.763
$Mn^{2+} + 2e \rightleftharpoons Mn$	− 1.180
$Al^{3+} + 3e \rightleftharpoons Al$	− 1.660
$Mg^{2+} + 2e \rightleftharpoons Mg$	− 2.370
$Na^{+} + e \rightleftharpoons Na$	− 2.714
$Ca^{2+} + 2e \rightleftharpoons Ca$	− 2.870
$Sr^{2+} + 2e \rightleftharpoons Sr$	− 2.890
$Ba^{2+} + 2e \rightleftharpoons Ba$	− 2.900
$K^{+} + e \rightleftharpoons K$	− 2.925
$Li^{+} + e \rightleftharpoons Li$	− 3.045

↓ Reduction of the metal ions becomes difficult

↓ Reducing ability of the metal ions increases

7.5.4. Utilities of Standard Reduction Potentials : The major utilities may be summarised as follows :

1. As we move down from Pt^{2+}/Pt ($E^\circ = +1.200$ volts) to the couple Li^{+}/Li ($E^\circ = -3.045$ volts) we find that the reduction potentials gradually get negative. This means it is far easier for lithium metal to release electron than it is for platinum. This means that the reducing ability of the *metals* increases with increasingly negative E° values. Conversely it becomes increasingly difficult to reduce the *metal ions* with increasingly negative E° values.

2. Since *platinum metal* releases electrons most reluctantly it means that *platinum ion* (high positive E°) accepts electrons most readily. So we conclude that the more positive the E° value is the easier it is to reduce the metal ion. Thus it is the most difficult to reduce the alkalies and the alkaline earths while it is far easier to reduce ions like copper (II), silver (I), mercury (II) etc.

3. The Table of standard reduction potentials easily allows us to predict the cell potentials. Algebraic addition of potentials of any two half-cells will give us the value of the cell potential. Thus the magnitude of the cell potential of the cell

obtained by combining the couples Zn^{2+}/Zn ($E^\circ = -0.763$ volts) and Cu^{2+}/Cu ($E^\circ = +0.337$ volts) gives a value $0.337 - (-0.763) = 1.1$ volts. This is the experimental *e.m.f.* of the Daniell cell. Similarly we can compute the *e.m.f.* of the cell obtained by coupling the two half-cells Cu^{2+}/Cu ($E^\circ = +0.337$ volts) and Ag^+/Ag ($E^\circ = +0.799$ volts) as $0.799 - 0.377 = 0.462$ volts. Since the silver couple is more positive the silver end has to be connected to the positive end of the potentiometer.

4. A scrutiny of the reduction potentials allows us to predict which displacement reaction is possible and which is not. For instance we reexamine the Daniell cell combination. Since zinc has a more negative E° value than copper it means that on introducing a zinc rod into a solution of copper (II) the zinc rod will release zinc (II) ions in solution and leave electrons on its surface. These electrons will reduce the copper (II) ions. The result is deposition of copper metal on the surface of zinc. On the contrary nothing will happen if we immerse a copper plate into a solution of zinc (II) ions. Even if we assume that copper (II) ions are formed leaving behind some electrons on its surface and these electrons reduce the zinc (II) ions to zinc metal, then the zinc metal will immediately come back to solution by virtue of its higher negative E° value. Thus we would see that if we introduce a copper rod ($E^\circ = +0.337$ volts) into a silver (I) solution ($E^\circ = +0.799$ volts) copper will dissolve to give the blue coloured copper (II) solution while metallic silver will be deposited on the surface of the copper metal. On the contrary no displacement reaction will be noticed if we immerse a silver wire into a solution of copper (II).

5. The couples which have very high negative E° values occur in nature in combined state eg. the alkalies, the alkaline earths etc. The couples which have high positive E° values sometimes occur in nature in element form eg. gold, mercury.

6. Hydrogen electrode is the reference point in the scale of standard reduction potentials. The elements above hydrogen have positive E° values. This means that these elements are less reluctant to release electrons than hydrogen itself *i.e.* these ions cannot reduce H^+ ion of acids to liberate hydrogen gas. On the other hand the elements with negative E° values readily release electrons and thus can reduce H^+ ion to liberate hydrogen gas from acids. Based on this distinction the following electrochemical series has been proposed :

Li, K, Ba, Sr, Ca, Na, Mg, Al, Mn, Zn, Fe, Cd, Co, Ni, Sn	H	Cu, Hg, Ag, Pd, Pt
These elements react with acids to liberate hydrogen.		These elements cannot liberate hydrogen from acids; they react only with oxidising acids like HNO_3.

7.5.5. Oxidation Reduction Potential : In the standard reduction potentials the half-cells comprise a metal ion and the corresponding metal. Instead if we take a solution comprising two ions of the same metal in two oxidation states and introduce an inert platinum wire the system will develop a potential and behave as a half-cell. If such a half-cell is connected with a standard hydrogen electrode through a potentiometer the recorded voltage will be the the standard oxidation-reduction potential of the half-cell. Following the rules laid down by the International Union of Pure and Applied Chemistry such oxidation-reduction reactions are written as :

$$\text{oxidant} + ne \rightleftharpoons \text{reductant}$$

The potential of such reactions is given by the following expression :

$$E = E^\circ - \frac{RT}{nF}\ln\frac{a_{\text{Red}}}{a_{\text{Ox}}} = E^\circ + \frac{RT}{nF}\ln\frac{a_{\text{Ox}}}{a_{\text{Red}}} = E^\circ + \frac{0.0591}{n}\log\frac{[\text{Ox}]}{[\text{Red}]}$$

where a stands for the activity of the species, n for the number of electrons transferred in the oxidation-reduction process and F for a Faraday. When both the reductant and the oxidant are at unit activity E equals E°. Some important standard oxidation-reduction potentials are given in Table 7.3. A scrutiny of this Table provides us the following general informations :

1. The lower the value of the standard oxidation-reduction potential the stronger the reductant is. Thus the E° values of the Sn^{4+}/Sn^{2+} and Fe^{3+}/Fe^{2+} are respectively + 0.15 and + 0.77 volts. This means Sn^{2+} is a stronger reducing agent than Fe^{2+}. Therefore Sn^{2+} is quite capable of reducing Fe^{3+}.

2. The higher the value of the oxidation-reduction potential the stronger the oxidant is. Compare the E° values of Br_2/Br^- and Fe^{3+}/Fe^{2+} couples: + 1.07 and + 0.77 volts. This indicates that bromine is a stronger oxidising agent than Fe^{3+}. Therefore bromine can oxidise ferrous to ferric but ferric cannot oxidise bromide ion. But ferric can and does oxidise iodide ion to iodine (E°, I_2/I^- ; 0.54 volts).

3. The oxidising abilities of fluorine, permanganate and dichromate are in the order : $F_2 > MnO_4^- > Cr_2O_7^{2-}$

Table 7.3. Standard Oxidation Reduction Potentials at 25°C

Oxidation-Reduction	Half Reaction	Standard Potential (Volts)
$F_2 + 2e$	$\rightleftharpoons 2F^-$	.... + 2.65
$S_2O_8^{2-} + 2e$	$\rightleftharpoons 2SO_4^{2-}$	.... + 2.01
$Ce^{4+} + e$	$\rightleftharpoons Ce^{3+}$	.... + 1.69
$MnO_4^- + 8H^+ + 5e$	$\rightleftharpoons Mn^{2+} + 4H_2O$	.... + 1.52
$Cl_2 + 2e$	$\rightleftharpoons 2Cl^-$	.... + 1.36
$Cr_2O_7^{2-} + 14H^+ + 6e$	$\rightleftharpoons 2Cr^{3+} + 7H_2O$	.... + 1.33
$Br_2 + 2e$	$\rightleftharpoons 2Br^-$	.... + 1.07
$Cu^{2+} + I^- + e$	$\rightleftharpoons CuI$	.... + 0.86
$Fe^{3+} + e$	$\rightleftharpoons Fe^{2+}$	.... + 0.77
$I_2 + 2e$	$\rightleftharpoons 2I^-$	.... + 0.54
$Sn^{4+} + 2e$	$\rightleftharpoons Sn^{2+}$	.... + 0.15
$2H^+ + 2e$	$\rightleftharpoons H_2$	.... + 0.00
$Cr^{3+} + e$	$\rightleftharpoons Cr^{2+}$	.... − 0.41

↑ Oxidising ability increases

Reducing ability increases ↓

7.6. ELECTRICAL ENERGY FORCES CHEMICAL REACTIONS : THE STORY OF ELECTROLYTIC CELL

We have so far seen how spontaneous chemical reactions can be utlised to produce electric energy. It is also possible to use electric energy to bring about non-spontaneous chemical reactions. Electrolytic reactions are chemical changes carried out through the application of external source of voltage *i.e.* electrical energy. *An electrolytic cell may be defined as a device where oxidation-reduction reactions are carried out by a direct electric current. The process going on inside such a cell is called electrolysis.*

A necessary and obvious condition for electrolysis to be fruitful is that the chemical to be electrolysed must itself be an electrolyte *i.e.* it must conduct direct electric current. In other words, the electrolyte must be an ionic compound composed of oppositely charged ions. Some of the often used electrolytes in industry are fused NaCl, cryolite, $CaCl_2$, $MgCl_2$ etc.

Now let us see what really goes on during an electrolytic process. Inside the electrolyte are dipped two conducting *electrodes.* One of these electrodes is connected to the negative end of the external source of direct current—may be a storage battery or the electric mains. The electrode connected to the negative end of the external source is the *cathode* of the electrolytic cell while the other end is the *anode*. The external source maintains an electron pressure on the cathode. The result is obvious : the positive cations in the electrolyte move closer to the negatively charged cathode. The cations take up electrons from the cathode, get neutralised and are deposited on the cathode surface or liberated at the cathode. As soon as this happens the anion, which has accumulated close to the anode, gives up its extra electron, gets neutralised and is liberated at the anode. Once again we see that *oxidation occurs at the anode and reduction at the cathode and that oxidation-reduction occurs simultaneously.*

The young reader should get one point straightened out : *electrons never travel through the electrolyte*. If this were true then the same electron would emerge from the external source, come to the cathode of cell, run through the electrolyte and finally be back again into the external source. This process would have continued for ages without there being any chemical decomposition. What actually occurs is that the external source of direct current maintains a pressure of electrons on the cathode surface. This leads to electrolysis.

7.6.1 Examples of Electrolytic Reactions : Two examples are discussed below:

1. *Electrolysis of fused sodium chloride :* Industrial preparation of sodium metal makes use of this reaction. Graphite anode is lowered into fused NaCl. The graphite anode is encircled by a circular iron anode. The graphite and the iron are connected to the positive and the negative ends of the electric mains. On closing the circuit electrolysis begins and oxidation and reduction reactions start at the anode and the cathode respectively.

$$NaCl \rightarrow Na^+ + Cl^-$$

at the cathode : $Na^+ + e \rightarrow Na$

at the anode : $2Cl^- \rightarrow Cl_2 + 2e$

The chlorine liberated at the anode is an important industrial product. We will have occasions to come across similar electrolytic procedures when we take up the descriptive chemistry of the elements.

2. *Electrolysis of aqueous* $1M$ *sodium chloride* : The first example was rather simple enough in that only two ions, namely sodium ion and chloride ion were involved. In aqueous solution we have two more ions to tackle, namely H^+ and OH^- ions. It is however true that compared to NaCl the solvent H_2O is far weaker an electrolyte: the concentration of the two ions (H^+ and OH^-) being of the order of 10^{-7} moles/litre. As against this the concentration of the sodium and the chloride ions is $1M$. But what is important here is the relative oxidation-reduction potentials:

$$\begin{aligned} Na^+ + e &\rightleftharpoons Na &;\quad E^\circ &= -2.714 \text{ volts} \\ Cl_2 + 2e &\rightleftharpoons 2Cl^- &;\quad E^\circ &= +1.36 \text{ volts} \\ 2H^+ + 2e &\rightleftharpoons H_2 &;\quad E^\circ &= 0.000 \text{ volts} \\ O_2 + 2H_2O + 4e &\rightleftharpoons 4OH^-(1\times10^{-7}M) &;\quad E^\circ &= +0.82 \text{ volts} \end{aligned}$$

The standard potentials of Na^+/Na and H^+/H_2 are respectively -2.714 and 0.000 volts. This means that it is lot more difficult to reduce Na^+ ion to Na atom than to get liberation of H_2 on the cathode. Again the standard potentials of Cl_2/Cl^- and O_2/OH^- are $+1.36$ and $+0.82$ volts respectively. Once again we find that it is easy enough to get discharge of oxygen at the anode than that of chlorine. In reality we do find that electrolysis of $1M$ aqueous NaCl leads to liberation of hydrogen at the cathode and oxygen at the anode instead of sodium and chlorine. In effect therefore electrolysis of $1M$ NaCl is electrolysis of water :

$$H_2O \rightleftharpoons H^+ + OH^-$$

at the cathode : $2H^+ + 2e \rightarrow H_2$

at the anode : $4OH^- \rightarrow 2H_2O + O_2 + 4e$

However we would like to point it out at this stage that on increasing the concentration of NaCl i.e. say to the stage of brine (saturated NaCl ; $6M$) electrolysis gives off chlorine at the anode and H_2 at the cathode. Liberation of H_2 at the cathode means concentration of OH^- ions around the cathode. On agitation and at lower temperature it may be possible to get the chlorine mixed up with the OH^- ion to produce hypochlorite ion, $HClO^-$. This is the basis of the industrial manufacture of sodium hypochlorite.

7.6.2. Faraday adds quantitative dimension to the phenomenon of electrolysis :

Faraday did a lot of studies with electrolysis of various electrolytes. These studies allowed him to propose two basic laws of electrolysis.

Faraday's First Law : The amount of the chemical reaction taking place at an electrode is directly proportional to the quantity of electricity passing through the electrolyte.

Quantity of electricity is expressed in terms of coulombs : number of coulombs = number of amperes × number of seconds

$$(Q) \quad = \quad (I) \quad \times \quad (t)$$

It is possible to determine the amount of the chemical deposition of a metal by weighing the cathode before and after the electrolysis experiment. Thus it is possible to know the amount of electricity that will be required to deposit one gram atom of an element from monopositive cations. This quantity of electricity is 96,500 coulombs, given a special name *Faraday*. One gram ion of monopositive cations contains a mole of that ions i.e. 6.023×10^{23} ions. Deposition of one gram ion in the form of neutral gram-atom will require 6.023×10^{23} electrons. Thus we see that a *Faraday* is in fact the total charge of one mole of electrons (Chapter 1).

Faraday's first law gives the following relation :

$$W \propto Q \;; \qquad \therefore W = ZQ$$

where W is the amount deposited or discharged at an electrode, Q is the total quantity of electricity and Z is the proportionality constant. It can be easily appreciated that the proportionality constant will assume two values depending on whether we take Q as one coulomb or a *Faraday*. When Q equals 1, W becomes equal to Z i.e. the proportionality constant represents the amount deposited or discharged at an electrode on the passage of one coulomb of electricity. This is the electrochemical equivalent of an element with respect to one coulomb. On the other hand when we take Q as a *Faraday* W i.e. Z represents the material deposited or discharged at an electrode on the passage of one *Faraday*. This amount is the electrochemical equivalent corresponding to one *Faraday* and will be the same as the chemical equivalent. Thus we have the following relation :

Chemical equivalent = Electrochemical equivalent corresponding to one *Faraday*
= Electrochemical equivalent corresponding to one coulomb × 96,500

Let us take an example :
Chemical equivalent of silver = 107.9 gram
Electrochemical equivalent of silver corresponding to one *Faraday* = 107.9 gram
Electrochemical equivalent of silver corresponding to one coulomb = 0.00118 gram
Electrochemical equivalent of silver corresponding to one *Faraday* = electrochemical equivalent of silver corresponding to one coulomb × 96,500 = 0.001118 × 96,500 gram = 107.9 gram.

Faraday's Second Law : *The amounts of different elements deposited or discharged at the electrodes are proportional to their electrochemical equivalents.*

Let us take the cases of two elements A and B. Their chemical equivalents i.e. more commonly called *gram equivalent weights* are E_A and E_B. Ionic compounds of these elements are electrolysed by the passage of the same quantity of electricity Q. If the amounts deposited or discharged at the cathode are W_A and W_B respectively, then the second law gives the following relations :

$$W_A = Z_AQ \;;\; W_B = Z_BQ \;;\; \therefore \frac{W_A}{W_B} = \frac{Z_A}{Z_B}$$

When Q is one *Faraday* then W's will be the chemical equivalents i.e. gram equivalent weights :

$$\frac{W_A}{W_B} = \frac{Z_A}{Z_B} = \frac{E_A}{E_B}$$

We know copper is bivalent while sodium is monovalent. So passage of one *Faraday* through fused NaCl and aqueous $CuSO_4$ will give one gram atom i.e. 23 gm of sodium but 63.5/2 i.e. 31.8 gm of copper at the cathode.

7.6.3. Some problems related to Faraday's laws of electrolysis

Problem 1 : A current of 3.00 amperes is passed through a concentrated copper (II) chloride solution for 10.00 hours. Calculate the amount of copper and chlorine liberated at the two electrodes.

number of coulombs = number of amperes × number of seconds
= $3.00 \times 10 \times 60 \times 60$
number of *Faraday* = $(3.00 \times 10 \times 60 \times 60)/96{,}500 = 1.12$ *Faraday*

One *Faraday* deposits one gram atom or gram equivalent as the case may be. In the case of copper (II) the ion is bipositive. Hence two *Faradays* will be required to deposit one gram atom. So one *Faraday* will deposit half gram atom or one gram equivalent of copper i.e. $63.5/2 = 31.8$ gram. Therefore 1.12 *Faraday* will deposit $1.12 \times 31.8 = 35.85$ gram of copper metal at the cathode.

Chloride ion is mononegative. Thus passage of one *Faraday* will liberate one gram atom of chlorine i.e. 35.5 gram at the anode. So 1.12 *Faraday* will cause the discharge of $1.12 \times 35.5 = 39.8$ gram of chlorine gas at the anode.

Problem 2 : A current of 40 ampere is passed through a solution of copper (II) sulphate for a period of six hours. Calculate the number of coulombs, number of *Faraday*, number of electrons involved and the amount of copper deposited at the cathode.

number of coulombs = number of amperes × number of seconds
= $40 \times 6 \times 60 \times 60$
number of *Faraday* = number of coulombs/96,500 = $(40 \times 6 \times 60 \times 60)/96{,}500$
= $(9 \times 96{,}000)/96{,}500 \simeq 9$ *Faraday*

One *Faraday* represents the charge carried by one mole of electrons i.e. 6.023×10^{23} electrons. Therefore the number of electrons involved in the electrolysis = $9 \times 6.023 \times 10^{23}$

One *Faraday* deposits one gram equivalent i.e. 31.8 gram of copper.

Therefore 9 *Faraday* will lead to the deposition of $9 \times 31.8 = 286.2$ gram

Problem 3 : Electrolysis of Al_2O_3 dissolved in molten cryolite gives aluminium at the cathode and oxygen at the anode. Determine the electrochemical equivalent of aluminium and oxygen (given : atomic weights of aluminium and oxygen are 26.97 and 16.00).

In molten cryolite Al_2O_3 functions as an ionic compound and dissociates into Al^{3+} and O^{2-} ions :

$$Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}$$

$$\text{at the cathode : } Al^{3+} + 3e \rightarrow Al$$

$$\text{at the anode : } O^{2-} \rightarrow O + 2e$$

Thus we see that the reduction of an aluminium ion is a three electron process. Therefore three *Faradays* will be required to deposit one gram atom i.e. 26.97 grams of aluminium at the cathode. Electrochemical equivalent of aluminium corresponding to one *Faraday* is 26.97/3 = 8.99 gram.

Oxidation of oxide ion at the anode is a two-electron process. Discharge of one gram atom i.e. 16.00 gram of oxygen will require two *Faradays*. Therefore the electrochemical equivalent weight of oxygen corresponding to one *Faraday* is 16.00/2 = 8.00 gram.

Problem 4 : 0.318 gram of copper was deposited at the cathode during electrolysis of copper (II) sulphate solution. The electrolysis was run for 20 minutes. Calculate the number of amperes, number of *Faradays*, number of electrons (at. wt of Cu = 63.5).

Since copper (II) is bipositive the electrochemical equivalent of the metal corresponding to one *Faraday* is 63.5/2 = 31.8 gram. Number of *Faraday* involved in the electrodeposition of 0.318 gram of copper = (0.318)/31.8 = 0.01 *Faraday*. 0.01 *Faraday* = 0.01 × 96,500 coulombs = 965 coulombs. But one coulomb is one ampere × one second. Therefore 965 coulombs = number of ampere × 20 × 60 = 0.8 ampere. One *Faraday* is the total charge carried by one mole i.e. 6.023×10^{23} electrons. Therefore 0.01 *Faraday* corresponds to 6.023×10^{21} electrons.

Problem 5 : How much silver would be deposited at the cathode if we use the same amount of electricity as in *Problem* 4 (atomic weight of silver = 107.9) Silver (I) is monopositive and hence one *Faraday* will deposit one gram atom of silver. We have already worked out the amount of electricity involved in the above problem.

Amount of silver deposited = number of *Faradays* × electrochemical equivalent of silver = 0.01 × 107.9 = 1.079 gram.

Problem 6 : A 14.0 square centimetre metal plate was silver plated to a thickness of 0.01 cm. A current of 0.012 ampere was passed through $KAg(CN)_2$ to get that deposit at the cathode (atomic weight of silver = 107.9 and density os silver = 10.5/cm³). Find the time.

Total amount of silver deposited = volume × density = 14.0 × 0.01 × 10.5 gm. = 1.47 gm.

One *Faraday* will give a deposit of 107.9 gm of silver. Therefore the number of *Faraday* required to deposit 1.47 gm = (1.47)/107.9 = 0.0136 *Faraday* 0.0136 *Faraday* = 0.0136 × 96,500 coulombs = 1312 coulombs. 1312 coulombs = number of amperes × number of seconds.

Number of seconds = 1312/0.012 = 109333 seconds

Time required = 109333/(60 × 60) hours = 30.4 hours

EXERCISES

1. Compare the classical definitions of oxidation and reduction with the electronic definitions.

2. The compound LiH is formed by the reaction of hydrogen and lithium metal at about 600°C. The fused compound on electrolysis gives hydrogen at the anode and lithium at the cathode. Show that while classical definition would call hydrogen a reducing agent in reality it is an oxidant in the formation of LiH.

3. What is oxidation number? Tabulate the oxidation numbers of the constituent elements in the following compounds :

$$HCl,\ CH_4,\ Na_2O_2,\ HF,\ F_2O,\ LiH$$

4. Write down the reaction between ferrous sulphate and potassium dichromate in acid medium and show from the count of the oxidation numbers of chromium and iron that the ferrous iron is the reducing agent and the dichromate is the oxidising agent.

5. Balance the redox reaction between $KMnO_4$ and $FeSO_4$ by the ion-electron method and the oxidation number method.

6. Give an example of an electrochemical cell. Explain in this context the terms : anode, cathode, electrolyte.

7. Explain the statement that oxidation occurs at the anode while reduction takes place at the cathode. Justify that this statement is true both in the cases of an electrochemical cell and an electrolytic cell.

8. The single electrode potentials of some half cells are given below. Indicate the cell potential when the half cells are connected :

$$\begin{array}{llll}
(a) & Cu^{2+} + 2e \rightleftharpoons Cu & ; E^0 = & 0.337 \text{ volts} \\
 & Zn^{2+} + 2e \rightleftharpoons Zn & ; E^0 = & -0.763 \text{ volts} \\
(b) & Al^{3+} + 3e \rightleftharpoons Al & ; E^0 = & -1.660 \text{ volts} \\
 & Mg^{2+} + 2e \rightleftharpoons Mg & ; E^0 = & -2.370 \text{ volts} \\
(c) & Cu^{2+} + 2e \rightleftharpoons Cu & ; E^0 = & 0.337 \text{ volts} \\
 & Ag^{+} + e \rightleftharpoons Ag & ; E^0 = & 0.799 \text{ volts}
\end{array}$$

Also indicate which of the metal electrodes will function as the anode and which one as the cathode. Indicate the flow of electrons in the outer circuit.

9. From a consideration of the single electrode potentials given in the preceding question answer the following questions :

(*a*) What will happen on immersing a zinc rod into a solution of cupric ions?
(*b*) What will happen if a copper rod is immersed in a solution of zinc ions?
(*c*) What will happen on immersing a copper plate in a solution of silver nitrate?
(*d*) Which metal is a stronger reducing agent in the pairs?
Zn/Cu ; Al/Mg ; Ag/Cu
(*e*) Which is the most reducing metal in the series : Zn/Cu/Al/Mg/Ag

10. Clearly distinguish between an electrochemical cell and an electrolytic cell.

11. Enunciate Faraday's laws of electrolysis. What is gram equivalent weight? How much metal will be deposited at the cathode on the passage of one *Faraday* of electricity through fused electrolytes of monovalent sodium, bivalent magnesium and trivalent aluminium. (atomic weights of sodium, magnesium and aluminium are 23, 24 and 27 respectively).

12. Give a clear exposition of the functioning of lead storage battery. State its behaviour as electrochemical cell or electrolytic cell during charging and discharging reactions. (see Chapter 18).

CHAPTER 8

ACIDS AND BASES

8.1. WE TAKE A LOOK INTO THE PAST

Acids and bases are today quite familiar terms even to nonscience people. As in many other fields our present-day knowledge has been a continuing improvement over older classical ideas. For the benefit of the young readers it may be quite in order to quote Lavoisier (1789) : "The acids are compounded of two substances—the one constitutes the acidity and is common to all acids while the other is peculiar to each acid and distinguishes it from the rest." Some common properties of the two classes of compounds called acids and bases allowed the earlier chemists to make the following tabulation :

Acids	*Bases*
1. Each acid contains hydrogen	1. Aqueous solution conducts electricity
2. Aqueous solution conducts electricity	2. Reacts with acids to counter acid properties
3. Reacts with zinc or magnesium to liberate hydrogen	3. Changes the colour of red litmus to blue
4. Changes the colour of blue litmus to red	4. Reacts with heavy metal salts to give insoluble precipitates
5. Tastes sour	5. Tastes bitter
	6. Gives a slippery feeling to the skin

There was a time when chemists thought that oxygen was inevitably a component of all acids. But then Davy demonstrated in 1890 that hydrochloric was an acid and yet had only hydrogen and chlorine.

Today with progressive advancement of science better and still better definitions of acids and bases are being sought. Instead of relying on some empirical properties, as outlined above, chemists have defined acids and bases in terms of the fundamental particle electron. For our benefit of understanding how the subject developed to the modern stage it is best to approach it the way it developed. We shall take up the three theories : (1) Arrhenius' theory (2) Lowry and Bronsted theory and (3) Lewis' theory. The three theories constitute a fine example of continuing improvement over existing ideas and a search towards a generalisation in terms of electronic structure of matter.

8.2. THEORIES OF ACIDS AND BASES

8.2.1. Arrhenius' theory : Arrhenius conducted voluminous studies on the passage of electricity through aqueous solutions of salts of different nature and concentrations. He concluded that the results could best be explained on the assumption that these aqueous solutions contained *charged species called ions*. He for the first time proposed definitions of acids and bases : *An acid is a substance which in aqueous solution produces a hydrogen cation* (H^+) *and an anion* ($HCl \rightarrow H^+ + Cl^-$). *A base is a substance which gives a negative hydroxide ion* (OH^-) *and a positively charged ion* ($NaOH \rightarrow Na^+ + OH^-$).

So revolutionary and startling these ideas were that Arrhenius was awarded the Doctorate at Upsala most reluctantly. Nobody cared to listen to his dissociation theory till he found a strong supporter in the great Ostwald. He travelled a lot to sell his ideas. His paper "On the Dissociation of Substances in Aqueous Solutions" finally appeared in 1889. Later in 1903 he was the third to receive the Nobel award in Chemistry. He was famous for his flair for making friendship. Although at the beginning he had to cope with tough opposition, he won the hearts of all great people of science. He had no foes but all good friends. Such was the personality of the Swede Svante August Arrhenius.

Nature of the hydrogen ion : All the studies of Arrhenius were conducted in aqueous medium. At his time not much was known about the electronic structure of the hydrogen atom and less so about the hydrogen ion. A hydrogen ion is a bare proton of the dimension of the nucleus i.e. 10^{-12} cm. Fajans' rules will tell us that such a small ion—indeed the smallest conceivable ion in the entire periodic table—will have the most deforming power. This is why the H^+ is readily protected by a H_2O molecule through a coordinate bond and takes the form $H^+(H_2O)$ i.e. H_3O^+. There is also a second opinion that the hydrated H^+ may have the formula $H^+(H_2O)_4$ (Fig. 8.1). However usually chemists use the H_3O^+ form or often for simplicity of representation just H^+. According to Arrhenius definition the following substances behave as acids because they liberate H^+ ion :

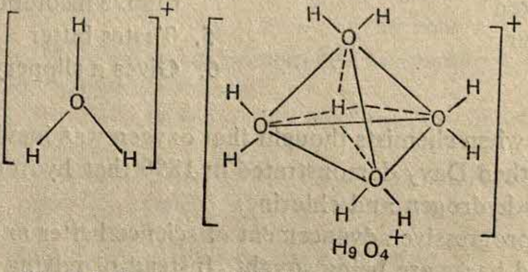


Fig. 8.1. Structures of H_3O^+ and $H_9O_4^+$ ions

$$HNO_3(aq) \rightarrow H^+ + NO_3^-$$
$$H_2SO_4(aq) \rightarrow H^+ + HSO_4^-$$
$$HCl(aq) \rightarrow H^+ + Cl^-$$

The following compounds are regarded as bases as they give OH^- ions in aqueous solution :

$$KOH(aq) \rightarrow K^+ + OH^-$$
$$Ba(OH)_2(aq) \rightarrow Ba^{2+} + 2OH^-$$

Arrhenius considered neutralisation as a process in which H^+ and OH^- combined to form water molecule :

$$H^+ + OH^- \rightarrow H_2O$$

8.2.2. Bronsted Lowry theory : With progress of chemical science examples started accumulating on acid-base type interactions in media other than water. Arrhenius restricted his theory solely to aqueous medium. *Bronsted-Lowry theory defined an acid as any species that can release a proton to another species and a base as a species that can accept a proton.* Thus the Bronsted-Lowry definition, in effect is *hydrogen-ion transfer* or *proton-exchange*. The young reader should not confuse this proton to be a proton of the nucleus of an atom.. The proton, we are talking about, is the hydrogen atom minus its valence electron i.e. H^+. This definition also brings along the idea of *conjugate base* and *conjugate acid*. A conjugate base is that part *of a species that remains after one or more protons are released. A conjugate acid is the species formed on the addition of one or more protons.* Thus each acid or a base may be considered to be made up of a pair of conjugate acid and a conjugate base. Thus when HCl breaks up into H^+ and Cl^- we can consider the chloride ion as the conjugate base because this can take up the H^+ ion to get back the acid HCl. We can conceive of adding one H^+ ion to H_2O to form H_3O^+. Then H_3O^+ is the conjugate acid of water. Again if we take off one H^+ ion from H_2O we are left with OH^- ion. Then OH^- ion is the conjugate base of water. A further interesting example is the bicarbonate HCO_3^- ion. If a H^+ ion is released we are left with the carbonate ion. Therefore the CO_3^{2-} ion is the conjugate base of HCO_3^- ion. But if we add a H^+ ion we get H_2CO_3. So H_2CO_3 can be regarded as the conjugate acid of HCO_3^- ion. Table 8.1 gives some common examples of conjugate acids and bases.

Table 8.1. Some Conjugate Acids and Bases

Acid	Conjugate Base	Base	Conjugate Acid
$HClO_4$	ClO_4^-	NH_3	NH_4^+
HCl	Cl^-	H_2O	H_3O^+
HNO_3	NO_3^-	OH^-	H_2O
H_2SO_4	HSO_4^-		
H_2CO_3	HCO_3^-	NH_2^-	NH_3
HCO_3^-	CO_3^{2-}	HS^-	H_2S

Bronsted-Lowry theory was a distinct improvement over Arrhenius theory because of the following points :

1. Solvent was not specified. Hence the definition could be extended to aqueous as well as non-aqueous solvents.

2. Arrhenius used H^+ and OH^- to define acids and bases. But the Bronsted-Lowry theory needed only H^+ ion to define both. In the case of acids withdrawal of H^+ ion and in the case of base addition of H^+ ion is necessary.

3. In Arrhenius theory neutralisation is the reaction between a H^+ ion and an OH^- ion. But in the Bronsted-Lowry theory acid base reaction is a competition between two bases for a proton. This is exemplified by the reactions between the following sets of pairs of conjugate acid-conjugate base (acid$_1$—base$_1$ and acid$_2$—base$_2$) :

Base$_1$		Acid$_2$		Acid$_1$		Base$_2$
NH_3	+	HCl	→	NH_4^+	+	Cl^-
OH^-	+	H_3O^+	→	H_2O	+	H_2O
CO_3^{2-}	+	H_3O^+	→	HCO_3^-	+	H_2O

8.2.3. Lewis Theory : G.N. Lewis will go down the memory lane for his extraordinary contributions in the area of electronic theory of valence. He realised that acid and base characters must be connected with the electronic structure of matter. It may be noted that although Bronsted-Lowry theory was a step forward compared to the Arrhenius theory, yet it was still limited because acidity and basicity could not arise in compounds having no hydrogen. Lewis proposed a most generalised definition : *A base is a substance that can donate an electron pair while an acid is a substance that can accept an electron pair.* This definition had nothing to do with the composition of the compound nor the solvent we are operating in. When NH_3 reacts with a H^+ ion to give NH_4^+ ion all that the base NH_3 does is to give its lone pair of electrons to the H^+ ion. Thus NH_3 is the electron-donor and hence the base, while the H^+ ion is the electron acceptor and hence the acid. An electron deficient molecule eg. BF_3 is thus an ideal Lewis acid. It is truism that there occurs a vigorous reaction between NH_3 and BF_3 to give the compound $F_3B \leftarrow NH_3$. We know that insoluble AgCl readily dissolves in ammonia to form $[Ag(NH_3)_2]^+$. Once again the monopositive silver ion is the Lewis acid while NH_3 is the base.

H^+	+	$:NH_3$	→	$[H \leftarrow NH_3]^+$
acid		base		product
F_3B	+	$:NH_3$	→	$[F_3B \leftarrow NH_3]$
acid		base		product
Ag^+	+	$2:NH_3$		$[H_3N \rightarrow Ag \leftarrow NH_3]^+$
acid		base		product

Lewis acids are often called electrophilic reagents (electron-seeking) while Lewis bases are called nucleophilic reagents (i.e. seeking nucleus poorly shielded by electron density). Given below are some species which are expected to exhibit Lewis acidity and basicity :

Lewis Acids	*Lewis Bases*
1. Cations	1. Anions
2. Molecules short of octet	2. Molecules with one or more lone pairs
3. Molecules with multiple bonds	3. Molecules with C = C bonds which are known to give overlap with metal ion orbitals eg. complexes with ethylene : $K[PtCl_3(C_2H_4)]$
4. Molecules which can expand their valence shells beyond octet	

8.3. ACID AND BASE PROPERTIES OF WATER

Most quantitative studies connected with acidity and basicity have been carried out in water. Water is basically a covalent compound. Even then it is known to dissociate to some extent. The dissociation constant of water is roughly of the order of 10^{-16} :

$$H_2O \rightleftharpoons H^+ + OH^- \,;\, K = \frac{[H^+]\,[OH^-]}{[H_2O]} \simeq 10^{-16}$$

In pure water at 25°C the molar concentration of hydrogen ions is around 10^{-7} and the product of $[H^+]\,[OH^-]$ is 10^{-14}. The concentration of undissociated H_2O molecules is 55.5 moles/litre. This huge concentration may be safely taken as constant compared to the concentration of H^+ and OH^- ions. The dissociation constant K multiplied by 55.5 is taken as the new constant K_w called the *ionic product of water.*

$$K_w = K \times [H_2O] = K \times 55.5 = 1.00 \times 10^{-14}$$

It has to be appreciated that whatever salts or acids or bases are dissolved in water the ionic product will always remain the same since this is a property of the solvent water itself. In pure water H^+ and OH^- ions are present to the equal extent i.e. 10^{-7} moles/litre in each case. This evidently leads to the K_w being 10^{-14}. But what would happen if we add some compound which gives fully dissociated H^+ ions. For example, HCl is fully dissociated in water. This means there will be a good amount of H^+ ions in aqueous solution. The concentrations of H^+ and OH^- ions are no longer the same. But K_w being a property of the medium the equilibrium so adjusts itself that the K_w remains the same 10^{-14}. If we take an aqueous solution which is 0.1 *M* in HCl we can assume that $[H^+]$ is also 0.1 *M* since aqueous HCl is totally dissociated into H^+ and Cl^- ions. In order to keep K_w constant the concentration of OH^- ions must go down as shown below :

$$K_w = [H^+]\,[OH^-] = 10^{-14} \,;\, \therefore\ [OH^-] = \frac{Kw}{[H^+]}$$

$$\therefore\ [OH^-] = \frac{1.00 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} M$$

On the other hand if we take $0.1M$ solution of KOH the solution will have $[OH^-]$ equal to $0.1M$. Again in order to keep the K_w constant we see that the $[H^+]$ does go down considerably—from 10^{-7} to $10^{-13}M$.

$$[H^+] = \frac{Kw}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}M$$

8.4. pH—A COMPACT EXPRESSION OF $[H^+]$

Handling of hydrogen ion concentration in terms of negative power of ten is undoubtedly cumbersome. Sorensen, a Danish chemist, hit upon the novel idea of expressing the H ion concentration as negative logarithm of the concentration. This manipulation expressed concentrations as very convenient positive numbers. Thus the H^+ ion concentration of water at 25°C is represented as :

$$pH = -\log_{10}[H^+] = -\log_{10}[10^{-7}] = -(-7) = +7$$

In the symbol pH the letter p stands for the Danish word *potenz* (power) while H stands for hydrogen. Thus pH *is the negative power of ten needed to express the hydrogen ion concentration in moles per litre.* We have just seen that the pH of a neutral solution is 7. In acidic solutions $[H^+]$ will be more than 10^{-7}, which means pH of acidic solutions will be below 7. For alkaline solutions the $[H^+]$ will be less than 10^{-7} so that the pH of alkaline solutions will be greater than 7.

As for $[H^+]$, the concentration of OH^- also can be expressed as pOH. Since neutral water has $[H^+]$ and $[OH^-]$ both at 10^{-7} it follows that $pH + pOH = 14$. It also follows that this sum will always remain constant. If pH goes up pOH will

Table 8.2. pH Scale

$[H^+]$	pH	$[OH^-]$	pOH	Acid/Base Character
10^0	0	10^{-14}	14	Acid
10^{-1}	1	10^{-13}	13	
10^{-2}	2	10^{-12}	12	
10^{-3}	3	10^{-11}	11	
10^{-4}	4	10^{-10}	10	
10^{-5}	5	10^{-9}	9	
10^{-6}	6	10^{-8}	8	
10^{-7}	7	10^{-7}	7	Neutral
10^{-8}	8	10^{-6}	6	Base
10^{-9}	9	10^{-5}	5	
10^{-10}	10	10^{-4}	4	
10^{-11}	11	10^{-3}	3	
10^{-12}	12	10^{-2}	2	
10^{-13}	13	10^{-1}	1	
10^{-14}	14	10^0	0	

Table 8.3. pH of Some Common Substances

Substance	pH	Substance	pH
Venegar	2.2	Human urine	7.4
Apple juice	3	Sea water	8.3
Tomato juice	4.2	0.1 M $NaHCO_3$	8.4
Carrot juice	5	Saturated $Mg(OH)_2$	10.5
Human saliva	5.7–7.1	0.1 M NH_4OH	11.2
Milk	6.6	0.1 M Na_2CO_3	11.6
		Saturated $Ca(OH)_2$	12.1

come down and vice versa. Above considerations allow us to sort out the following relations :

$$[H^+]\,[OH^-] = Kw = 10^{-14}$$

$$\therefore \quad \log[H^+] + \log[OH^-] = \log(10^{-14}) = -14$$

$$\therefore \quad -\log[H^+] - \log[OH^-] = -(-14) = 14$$

$$\therefore \quad pH + pOH = 14$$

Neutral solution : $[H^+] = [OH^-] = (10^{-14})^{\frac{1}{2}} = 10^{-7}M$
Acidic solution : $[H^+] > [OH^-]$; $[H^+] > 10^{-7}M$; $[OH^-] < 10^{-7}M$
Alkaline solution : $[OH^-] > [H^+]$; $[OH^-] > 10^{-7}M$; $[H^+] < 10^{-7}M$
Therefore we have :
Neutral solution : $[H^+] = 10^{-7}M$; $pH = 7.0$
Acidic solution : $[H^+] > 10^{-7}M$; $pH < 7.0$
Alkaline solution : $[H^+] < 10^{-7}M$; $pH > 7.0$

The interrelations of $[H^+]$, pH, $[OH^-]$ and pOH are depicted in table 8.2. Table 8.3 gives the pH of some substances of interest.

According to Sorensen the pH of a solution of $[H^+] = 1$ is zero. When the $[H^+]$ goes up above $1M$ the pH, of necessity, has to be negative. Such solutions are quite concentrated in H^+ ion and are not likely to be fully dissociated. Moreover talking in terms of negative figures makes little sense. In such cases the H^+ ion concentration is expressed in terms of molarity.

Problem 1 : Find the pH of the two solutions : (a) 0.015 M HCl and (b) 0.0025M $Ba(OH)_2$

(a) 0.015 M HCl : Hydrochloric acid is a monobasic strong acid. So it is fully dissociated in solution.

$$[H^+] = 0.015\,M = 15 \times 10^{-3}$$

$$pH = -\log[H^+] = -\log(15 \times 10^{-3}) = -\log 15 - \log(10^{-3})$$

$$= -\log 15 + 3\log 10 = -1.1761 + 3 = 1.82$$

(b) Barium hydroxide is a diacidic strong base. Its hydroxide ion concentration therefore will be double the concentration of $Ba(OH)_2$.

$[OH^-] = 2 \times 0.0025\,M$; $pOH = -\log(5 \times 10^{-3}) = -\log 5 + 3 \log 10$
$= -0.6990 + 3 = 2.30$

But we know $pH + pOH = 14$; $pH = 14 - 2.30 = 11.70$

Problem 2 : Calculate the concentrations of the H^+ and OH^- ions of a solution of pH 2.63.

$pH = -\log(H^+] = 2.63$; $\log[H^+] = -2.63 = \bar{3}.37$

Therefore $[H^+]$ = antilog of $\bar{3}.37 = 2.34 \times 10^{-3}$

Again $pH + pOH = 14$. Therefore $pOH = 14 - 2.63 = 11.37$

$pOH = -\log[OH^-] = 11.37$; $\therefore \log[OH^-] = -11.37 = \bar{12}.63$

concentration of $OH^- = [OH^-]$ = antilog of $\bar{12}.63 = 4.27 \times 10^{-12}$ gram ion/litre

Problem 3 : Calculate the pH of a solution containing 0.008 gram ion/litre of OH^- ions.

concentration of $OH^- = [OH^-] = 0.008$ gram ion/litre $= 8 \times 10^{-3}$

Therefore $pOH = -\log[OH^-] = -\log 8 + 3 \log 10 = -0.9031 + 3 = 2.097$

But $pH + pOH = 14$; $pH = 14 - 2.097 = 11.9$

Problem 4 : 50.00 ml of 0.100*M* HCl is being titrated with 0.100*M* NaOH solution. Calculate the pH values of the solutions at (a) the beginning (b) after addition of 10.00 ml of the NaOH solution and (c) after the addition of 60.00 ml of the alkali solution.

(a) *pH at the beginning* :

$[H^+] = 0.100\,M = 10^{-1}\,M$; $pH = -\log(10^{-1}) = 1.00$

(b) *after the addition of* 10.00 *ml of the alkali solution*

After addition of the alkali solution the volume becomes $10 + 50 = 60$ ml concentration of the acid $= [H^+] = [(50-10) \times 0.100\,M]/60 = 0.0666\,M$

$pH = -\log[H^+] = -\log(0.0666) = -\log(66.6010^{-3})$
$= -\log 66.6 + 3 = -1.8235 + 3 = 1.18$

(c) *after the addition of* 60.00 *ml of the alkali solution*

After the addition of the alkali solution the volume becomes equal to $60 + 50 = 110$ ml. Since both the acid and the alkali are strong we can safely assume that after neutralisation there remains in the solution an excess of 10 ml of 0.100*M* NaOH solution.

$[OH^-] = (10 \times 0.100)/110 = 9.09 \times 10^{-3}$; $pOH = -\log 9.09 + 3 = 2.04$

$pH + pOH = 14$; $pH = 14 - 2.04 = 11.96$

8.5. STRONG AND WEAK ACIDS

These two classes of acids are recognised by the extent of their dissociation in aqueous medium. The strong acids behave as strong electrolytes by being fully dissociated while the weak acids behave as weak electrolytes and are dissociated only partially. For weak acids the dissociation attains equilibrium and most of the acid molecules remain in their undissociated form. For strong acids the dissociation is complete and immeasurably high. Following are the distinguishing features of these two classes of acids :

Strong Acids	*Weak Acids*
1. Fully dissociated	1. Partially dissociated
2. Highly conducting	2. Poorly conducting
3. Very low pH	4. pH comparatively high
4. Liberates H_2 on reaction with Zn, Mg	5. Reaction with Zn, Mg is poor and very slow

8.6. DISSOCIATION CONSTANT OF WEAK ACIDS

For strong acids dissociation constants are immeasurably high. For weak acids however it is possible to measure the resulting pH and from the pH it is quite convenient to have a reliable value of the dissociation constant of the weak acid.

For a weak monobasic acid HX we can write the following relations :

$$HX \rightleftharpoons H^+ + X^- \; ; \; K_A = \frac{[H^+]\,[X^-]}{[HX]}$$

The H^+ ion in the above expression, however, will take the form of H_3O^+ in aqueous medium. The equilibrium constant, K_A, called the *acid dissociation constant* or *the ionisation constant*, will be independent of any added H^+, X^- or HX. The system will so respond in the presence of the added ions that the equilibrium constant remains the same. It is a manifestation of the well known Le Chatelier principle. If we add extra H^+ ion the system will so behave that it will oppose the new imposed constraint. All this means that the extra H^+ ion will link up with X^- to form undissociated HX i.e. dissociation of the weak acid HX will be restricted. Similarly if we add more X^- ions then the added X^- ions will add up with the H^+ ion to form undissociated HX. The over-all effect is that the dissociation constant will be maintained constant.

We will now briefly devote to the method of determining the K_A. In modern days there are in fact a host of very good methods to calculate out this constant. With the background that we have so far developed we can only talk of a very simple method only. We know what a hydrogen electrode is. It is a half-cell H^+/H_2 whose potential has been taken as 0.000 volts. If we make several half-cells containing H^+ ion of different concentrations and connect them in turn with the standard hydrogen electrode we will get cells where one half-cell is under standard condition (i.e. 1*M* H^+ ion). We will get a standard straight line when we plot the *e.m.f.* of these cells against the known H^+ ion concentration. An aqueous solution of HX of known strength is prepared and into this solution is dipped a Pt electrode and hydrogen gas is bubbled through under standard condition (i.e. 1 atm). This now constitutes a half-cell where the source of H^+ ion is the dissociation of the weak acid itself. This half cell is then connected with the standard hydrogen electrode and the *e.m.f.* of the cell is recorded with the help of a potentiometer. With the help of the calibration curve that we have prepared earlier we can find out what concentration of H^+ ion is given by the acid HX. Assuming this $[H^+]$ ion to be x, we find easily that $[X^-]$ is also x. If the original weighed out concentration of the HX is y, then the concentration of the undissociated HX in the denominator of the equilibrium equation should be given by $y - x$. Since the acid is a weak one we can safely drop the x in the denominator. Thus the K_A is given by :

$$K_A = \frac{[H^+]\,[X^-]}{[HX]} = \frac{x \times x}{y - x} = \frac{x^2}{y}$$

Problem 1 : 0.5 mole of HF is dissolved to give a 500 ml. solution. The $[H^+]$ of this solution is found to be $2.6 \times 10^{-2} M$. Calculate the dissociation constant of the acid.

Concentration of the HF solution = $(0.5 \times 1000)/500 = 1.0M$. Since the acid is a monobasic one the concentrations of H^+ ion and F^- will be the same. Concentration of undissociated HF is given by $(1.00 - 2.6 \times 10^{-2})M = 1.00M - 0.026M = 0.97\,M$

$$HF \rightleftharpoons H^+ + F^- \;;\; K_A = \frac{[H^+]\,[F^-]}{[HF]}$$

$$K_A = \frac{(2.6 \times 10^{-2}) \times (2.6 \times 10^{-2})}{0.97} = 7.0 \times 10^{-4}$$

Problem 2 : The dissociation constant of HF is 7.0×10^{-4}. Calculate the $[H^+]$ of a 0.100 M solution.

$$K_A = \frac{[H^+]\,[F^-]}{[HF]} \;;\; \text{taking } [H^+] = x,\; K_A = \frac{x^2}{0.100 - x} = 7.0 \times 10^{-4}$$

In order to simplify solving, x in the denominator is disregarded.
Then $x^2 = 0.100 \times 7.0 \times 10^{-4} = 70 \times 10^{-6}$
Therefore $x = [H^+] = 8.4 \times 10^{-3} M$

Problem 3 : The dissociation constant of NH_4Cl is 5.6×10^{-10}. Calculate the pH of 0.10 M aqueous solution

$$NH_4Cl \rightarrow NH_4^+ + Cl^- \;;\; NH_4^+ \rightleftharpoons NH_3 + H^+ \;;$$

$K_A = \frac{[NH_3]\,[H^+]}{NH_4Cl}$; taking the equilibrium concentration of H^+ ion as x

we have $K_A = \frac{x^2}{NH_4Cl} = 5.6 \times 10^{-10}$

Since the value of K_A is low we can safely take the concentration of the undissociated NH_4Cl as that at the beginning.

$$\text{Therefore } \frac{x^2}{0.1} = 5.6 \times 10^{-10} \quad \text{whence } x^2 = 56 \times 10^{-12}$$

$$[H^+] = x = 7.5 \times 10^{-6}M$$

$$\text{Finally the pH of the solution } = -\log(7.5 \times 10^{-6}) = -\log 7.5 + 6$$
$$= -0.8751 + 6 = 5.12$$

8.7. HENDERSON EQUATION

We have so far seen how we can find out the acid dissociation constant of a weak acid. The K_A is a characteristic of a particular acid. This remains constant even in the presence of added H^+ ion or the conjugate anion. The pH of a solution of such a weak acid is however dependent on the concentration of the externally added acid or a salt containing the conjugate anion. Henderson equation allows us to calculate the pH of an aqueous solution of a weak acid HA in presence of a salt containing the conjugate anion of the acid. Let us study the system containing HA and a salt MA. The compound MA being a salt is completely dissociated into M^+ and A^- ions. But the dissociation of HA will be dictated by its acid dissociation constant. We can write the following relations in respect of the pure acid :

$$HA \rightleftharpoons H^+ + A^- \ ; \quad K_A = \frac{[H^+]\,[A^-]}{[HA]} \ ; \quad \therefore \ [H^+] = \frac{[HA]}{[A^-]} \times K_A$$

We have already mentioned that the dissociation constant of a weak acid will remain intact even in the presence of added H^+ or A^- ions. Let us assume that the concentrations $[HA] = C_A$ and $[MA] = C_S$. Then the amount of undissociated HA will be given by :

$$[HA] = \text{concentration of initial HA} - \text{concentration of } H^+$$
$$= C_A - [H^+]$$

Amount of dissociated A^-

$$= [A^-] \text{ from the dissociation of MA} + [A^-] \text{ from the dissociation of HA}$$
$$= C_S + [H^+]$$

$$\text{Therefore } [H^+] = \frac{[HA]}{[A^-]} \times K_A = \frac{C_A - [H^+]}{C_S + [H^+]} \times K_A$$

Since we are dealing with a weak acid HA the value of $[H^+]$ will be small compared to the values of C_A and C_S. The above relation then simplifies to the following form :

$$[H^+] = \frac{C_A}{C_S} \times K_A = K_A \times \frac{[\text{Acid}]}{[\text{Salt}]}$$

Taking logarithms we have :

$$pH = -\log[H^+] = -\log K_A - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$pH = pK_A + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

This is the common form of the Henderson equation. When an acid HA is half-neutralised we have [Acid] = [Salt] so that log ([Salt]/[Acid]) becomes zero and hence pK_A is obtained directly from the pH of the solution. This equation further tells us that the pH of a weak acid depends upon the concentration of the salt of that acid present in solution.

Problem 1 : A solution is 0.1 N in acetic acid and also 0.1 N in sodium acetate. Calculate the pH of the solution (given $K_A = 1.82 \times 10^{-5}$).
The system contains a weak acid and its salt so that Henderson equation will be applicable.

$$\text{pH} = \text{p}K_A + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log(1.82 \times 10^{-5}) + \log(0.1/0.1)$$

$$= -\log 1.82 + 5 + 0.0 = 4.74$$

Problem 2 : To 1 litre of a solution which is 0.1 N both in acetic acid and sodium acetate 10 ml. of 1 N HCl is added. Calculate the pH of the solution. (K_A of $CH_3COOH = 1.82 \times 10^{-5}$).

The present system consists of a weak acid acetic acid, its sodium salt and a completely dissociated HCl. Henderson equation will be applicable. The H^+ ion resulting from the dissociation of HCl will attach itself to the acetate ion according to the Le Chatelier principle. The total acetate ion will be less than that expected from the complete dissociation of sodium acetate by the same amount that dissociated H^+ ion gets attached to the acetate ion.

concentration of H^+ ion $= 10/(1000 + 10) \simeq 0.01\ N$
concentration of CH_3COO^- ion $= 0.1 - 0.01 = 0.09\ N$
concentration of $CH_3COOH = 0.1 + 0.01 = 0.11$

According to Henderson equation : $\text{pH} = \text{p}K_A + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

$$= -\log(1.82 \times 10^{-5}) + \log \frac{0.09}{0.11}$$

$$= 4.74 - 0.09 = 4.65$$

8.8. HYDROLYSIS

In order to be able to appreciate what we really mean by hydrolysis we have to look into the neutralisation of some acids and bases and the resulting pH of the neutralised solution. Neutralisation of NaOH by HCl produces NaCl and H_2O. NaCl is a salt made out of a strong acid HCl and a strong base NaOH. NaCl does not react with water to produce any acid or alkali. Such salts dissociate into the component ions without being influenced by the solvent water. But the case with other salts is not as simple as that of NaCl. In the neutralisation of (a) weak acid and strong base (b) strong acid and weak base and (c) weak acid and weak base completely different situations prevail. In these cases this is a reality that even if equivalent amounts of acid and base are used in the neutralisation the pH at the equivalence point is not 7 — the pH we get in the neutralisation of HCl by NaOH at the equivalence point. This can only mean that the salt formed as a result of neutralisation reacts further with the solvent water to produce either a strong base or a strong acid. Let us have a look at the neutralisation of CH_3COOH by NaOH. At the equivalence point the pH is above 7. This is possible because the Na salt produced reacts with water to produce the strong base NaOH and the weak acid CH_3COOH :

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$
$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

The NaOH being a strong base releases OH^- ions at the equivalence point so that in reality we do find that the pH is above 7. On the contrary the neutralisation of the strong acid HCl with the weak base NH_4OH produces at the equivalence point NH_4Cl which reacts with the solvent water to give the strong acid HCl. The obvious result is that the pH at the equivalence point is below 7.

$$NH_4OH + HCl \rightleftharpoons NH_4Cl + H_2O$$
$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

Hydrolysis may be defined as a process whereby salts of weak acids or weak bases react with water to produce strong bases or strong acids. The general hydrolysis reaction may be expressed as :

$$\underset{\text{salt}}{MA} + \underset{\text{water}}{H_2O} \rightleftharpoons \underset{\text{base}}{MOH} + \underset{\text{acid}}{HA}$$

1. Salts of weak acids (eg. CH_3COONa) produce strong base (NaOH) and weak acid (CH_3COOH).

2. Salts of weak bases (eg. NH_4Cl) give weak base (NH_4OH) and strong acid (HCl).

8.8.1. Hydrolysis of a Salt of Weak Acid and Strong Base : We now look into the hydrolysis of a salt MA made of a weak acid HA and a strong base MOH. On dissolution in water the salt will first break up into the ions M^+ and A^-. The anion A^-, being the conjugate base of the weak acid HA, will react with water to give HA and OH^- ion.

$$MA \rightleftharpoons M^+ + A^- \,;\, A^- + H_2O \rightleftharpoons HA + OH^- \,;\, K_h = \frac{[OH^-][HA]}{[A^-]}$$

where K_h is the hydrolysis constant. We can use this equation to calculate out the degree of hydrolysis of the salt MA. Let us assume that 1 gram mole of the salt is dissolved in v litres of solution and let us assume that x is the degree of hydrolysis. Then the following relations in terms of v and x will hold :

$$\underset{(1-x)/v}{A^-} + H_2O \rightleftharpoons \underset{x/v}{OH^-} + \underset{x/v}{HA}$$

$$\text{Therefore } K_h = \frac{(x/v)\ (x/v)}{(1-x)/v} = \frac{x^2}{(1-x)/v}$$

Since K_h is a constant characteristic of the salt MA it follows that as v increases so also x. That is, *with increasing dilution the degree of hydrolysis will also increase.* With weak acids x is a small fraction of 1. So the above relation further simplifies to :

$K_h = x^2 . C$; $x = \sqrt{K_h/C}$ (C = concentration in moles per litre of MA) We will now demonstrate that the hydrolysis constant is intimately connected to the acid dissociation constant of the weak acid HA. Consider the following equilibria :

$$H_2O \rightleftharpoons H^+ + OH^- \quad ; \quad K_w = [H^+]\,[OH^-]$$

$$HA \rightleftharpoons H^+ + A^- \quad ; \quad K_A = \frac{[H^+]\,[A^-]}{[HA]}$$

Therefore the following manipulations can be made :

$$K_h = \frac{[OH^-]\,[HA]}{[A^-]} = \frac{K_w}{[H^+]} \cdot \frac{[H^+]\,[A^-]}{K_A\,[A^-]} = \frac{K_w}{K_A}$$

The concentrations of HA and OH^- arising out of the hydrolysis of the salt MA will be the same. If the concentration of MA be C gram moles per litre then we have :

$$K_h = \frac{[OH^-]\,[HA]}{[A^-]} = \frac{[OH^-]^2}{C} = \frac{K_w}{K_A}$$

$$\therefore\ [OH^-] = \sqrt{C\,K_w/K_A}$$

$$\text{Again } [H^+] = K_w/[OH^-] = \sqrt{K_w .\ K_A/C}$$

$$\therefore \quad \log\,[H^+] = \tfrac{1}{2}\log\,(K_w .\ K_A/C)$$

$$\therefore \quad pH = \tfrac{1}{2}\,pK_w + \tfrac{1}{2}\,pK_A + \tfrac{1}{2}\log C$$

Problem 1 : Determine the hydrolysis constant and pH of $0.1M$ sodium acetate (K_A of $CH_3COOH = 1.82 \times 10^{-5}$)

$$K_h = \frac{K_w}{K_A} = \frac{1.0 \times 10^{-14}}{1.82 \times 10^{-5}} = 5.5 \times 10^{-10}$$

$$\begin{aligned} pH &= \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_A + \tfrac{1}{2}\log C \\ &= 7 + \tfrac{1}{2}(-\log 1.82 \times 10^{-5}) + \tfrac{1}{2}\log(0.1) \\ &= 7 + 2.37 + \tfrac{1}{2}(-1) = 8.87 \end{aligned}$$

We can also calculate the degree of hydrolysis.

$$K_h = \frac{x^2}{(1-x)v}\ ; \quad \text{concentration} = = C\ \frac{1}{v}$$

$$= \frac{x^2 . C}{(1-x)} = \frac{x^2 \times 0.1}{(1-x)} = 5.5 \times 10^{-10}$$

Since x is small compared to 1, we have :

$$x^2 = 5.5 \times 10^{-10} \times 10^1 = 55 \times 10^{-10}\ ; \quad \therefore\ x = 7.6 \times 10^{-5}$$

Problem 2 : pH of 0.1 *N* acetic acid is 2.87. Determine the dissociation constant and degree of hydrolysis of the acid.

$$\mathrm{pH} = -\log[\mathrm{H}^+[= 2.87 \;;\quad \log[\mathrm{H}^+[= -2.87 = 3.\overline{13}$$

$$\therefore\ [\mathrm{H}^+] = \text{antilog of } 3.13 = 1.35 \times 10^{-3}$$

$$K_A = \frac{[\mathrm{H}^+]\,[\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]} = \frac{(1.35 \times 10^{-3}) \times (1.35 \times 10^{-3})}{0.1} = 1.8 \times 10^{-5}$$

If x is the degree of hydrolysis, then we can write :

$$K_h = \frac{x^2 \times 0.1}{1-x} = \frac{x^2 \times 0.1}{1} = \frac{K_w}{K_A} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} \;;\quad \therefore\ x = 7 \times 10^{-5}$$

Percentage hydrolysis = degree of hydrolysis × 100 = $7 \times 10^{-5} \times 10^2 = 0.007\,\%$.

8.8.2. Hydrolysis of a Salt of a Strong Acid and a Weak Base : Let us consider the case of a salt MA where M^+ is the weak cation and HA is the strong acid. Since A^- is the conjugate base of the strong acid (eg : Cl^-, $\mathrm{NO_3}^-$) it will not react with the solvent water. But M^+ will undergo hydrolysis. The following equilibria will exist :

$$\mathrm{MA} \rightleftharpoons \mathrm{M}^+ + \mathrm{A}^- \;;\quad \mathrm{M}^+ + \mathrm{H_2O} \rightleftharpoons \mathrm{MOH} + \mathrm{H}^+$$

Then $$K_h = \frac{[\mathrm{MOH}]\,[\mathrm{H}^+]}{[\mathrm{M}^+]} \;;\quad \text{Again } K_w = [\mathrm{H}^+]\,[\mathrm{OH}^-]$$

$$K_B = \frac{[\mathrm{M}^+]\,[\mathrm{OH}^-]}{[\mathrm{MOH}]} \quad (\text{since } \mathrm{MOH} \rightleftharpoons \mathrm{M}^+ + \mathrm{OH}^-)$$

Therefore :

$$K_h = \frac{K_w}{K_B} = \frac{[\mathrm{H}^+]^2}{C} \quad (\text{since } [\mathrm{MOH}] = [\mathrm{H}^+] = [\mathrm{M}^+] = C)$$

$$\therefore \qquad [\mathrm{H}^+] = \sqrt{C \,.\, K_w/K_B}$$

$$\therefore \qquad \log[\mathrm{H}^+] = \tfrac{1}{2}\log C + \tfrac{1}{2}\log K_w - \tfrac{1}{2}\log K_B$$

Then $$\mathrm{pH} = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_B - \tfrac{1}{2}\log C$$

Problem 1 : Calculate the pH of an aqueous solution of 0.1 *N* $\mathrm{NH_4Cl}$ (given K_B of $\mathrm{NH_4OH} = 1.8 \times 10^{-5}$)

K_B of $\mathrm{NH_4OH} = 1.8 \times 10^{-5}$; $pK_B = -\log K_B = -\log(1.8 \times 10^{-5})$

$= -\log 1.8 + 5 = 4.74$

$$\mathrm{pH} = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_B - \tfrac{1}{2}\log C$$
$$= \tfrac{1}{2}(14) - \tfrac{1}{2}(4.74) - \tfrac{1}{2}\log(0.1) = 7 - 2.37 + 0.5 = 4.13$$

Problem 2 : Calculate the hydrolysis constant and degree of hydrolysis of 0.1*N* $\mathrm{NH_4Cl}$ (given $K_B = 1.8 \times 10^{-5}$)

$$K_h = \frac{K_w}{K_B} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.4 \times 10^{-10}$$

But $$K_h = \frac{x^2}{(1-x)v} = x^2.C \text{ (cf : section 8.8.1)}$$

$$\therefore \quad x = \sqrt{K_h/C} = \sqrt{5.4\times10^{-10}\times10^1}$$

$$= \sqrt{54\times10^{-10}} = 7.6\times10^{-5}$$

8.8.3. Hydrolysis of a Salt of Weak Acid and a Weak Base : Both the metal ion and the anion of such a salt MA will be velnerable to hydrolysis. Thus we will get both the hydroxide MOH and the acid HA besides the metal ion and the acid anion :

$$MA \rightleftharpoons M^+ + A^-$$

$$M^+ + A^- + H_2O \rightleftharpoons MOH + HA$$

$$K_h = \frac{[MOH]\,[HA]}{[M^+]\,[A^-]}\,;\quad K_w = [H^+]\,[OH^-]\,;\quad K_B = \frac{[M^+]\,[OH^-]}{[MOH]}$$

$$K_A = \frac{[H^+]\,[A^-]}{[HA]}\,;\quad K_h = K_w/(K_A\times K_B)$$

Therefore $$\log K_h = \log K_w - \log K_A - \log K_B$$

$$pK_h = pK_w - pK_A - pK_B$$

$$[H^+] = \frac{K_A\,[HA]}{[A^-]} = K_A\sqrt{K_h} = \sqrt{(K_w\times K_A)/K_B}$$

Thus $$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_A - \tfrac{1}{2}pK_B$$

We can also express the hydrolysis constant in terms of degree of hydrolysis i.e. the fraction of one gram mole of the salt undergoing hydrolysis. Assuming that one gram mole of the salt MA is dissolved in v litres of solution and x is the degree of hydrolysis we can write :

$$K_h = \frac{(x/v)\,(x/v)}{[(1-x)/v]^2} = \frac{x^2}{(1-x)^2} = \left(\frac{x}{1-x}\right)^2$$

Problem 1 : Calculate the pH of solutions of ammonium acetate and ammonium formate (given K_B of ammonia $= 1.8\times10^{-5}$; K_A of acetic and formic acids are respectively 1.8×10^{-5} and 1.77×10^{-4}).

pH of ammonium acetate $= \frac{1}{2}pK_w + \frac{1}{2}pK_A - \frac{1}{2}pK_B$

$= \frac{1}{2}(14) + \frac{1}{2}(4.74) - \frac{1}{2}(4.74) = 7.0$ (pK_B of ammonia $= 4.74$)

(pK_A of acetic acid $= 4.74$)

pH of ammonium formate

$= \frac{1}{2}pK_w + \frac{1}{2}pK_A - \frac{1}{2}pK_B$ (pK_A of formic acid $= 3.75$)

$= \frac{1}{2}(14) + (3.75) - \frac{1}{2}(4.74)$

$= 6.51$

Problem 2 : Calculate the hydrolysis constant and the degree of hydrolysis of ammonium formate (K_A of formic acid $= 1.77 \times 10^{-4}$ and K_B of ammonia $= 1.8 \times 10^{-5}$)

$$K_h = K_w/(K_A \times K_B) = \frac{1 \times 10^{-14}}{(1.77 \times 10^{-4})\,(1.8 \times 10^{-5})} = 3.0 \times 10^{-6}$$

Again $$K_h = \left(\frac{x}{1-x}\right)^2 ; \frac{x}{1-x} = \sqrt{K_h} = (3 \times 10^{-6})^{\frac{1}{2}} = 1.73 \times 10^{-3}$$

Neglecting the x term in the denominator we have $x = 1.73 \times 10^{-3}$

8.8.4. A critique of the hydrolysis equations : The pH values of the solutions in the three cases discussed above are summarised below :

Case I. Salt of weak acid and strong base :

$$\mathrm{pH} = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_A + \tfrac{1}{2}\log C$$

Case II. Salt of strong acid and weak base

$$\mathrm{pH} = \tfrac{1}{2}K_w - \tfrac{1}{2}pK_B - \tfrac{1}{2}\log C$$

Case III. Salt of weak acid and weak base :

$$\mathrm{pH} = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_A - \tfrac{1}{2}pK_B$$

Hydrolysis of a salt of weak acid and strong base will give an alkaline pH. Hence the pH equation has all plus signs. Hydrolysis of a salt of strong acid and weak base will give acidic i.e. lower pH and hence two minus signs appear in the pH equation. For the third case the most important point to note is that there is no term containing the concentration of the salt. The pH in this case is independent of the concentration of the salt. But in the former two cases the pH is concentration dependent. For example in case I the pH of 0.1 *M* and 0.01 *M* sodium acetate are 8.87 and 8.37 respectively. Also the more dilute the solution the more is the degree of hydrolysis.

8.8.5. Interrelations between K_A, pK_A and between K_B and pK_B : The acidity of different acids are expressed in terms of their K_A and pK_A while the basicity of the different bases are indicated by their K_B and pK_B. As K_A increases pK_A decreases and vice versa. The following data will substantiate the conclusion :

Acid	HF	>	CH_3COOH	>	H_3BO_3
K_A	7.0×10^{-4}		1.8×10^{-5}		5.8×10^{-10}
pK_A	3.2		4.7		9.2

Similar relation holds for K_B and pK_B although these values are less encountered.

8.9. ACID BASE NEUTRALISATION

We have investigated hydrolysis reactions of salts of acids and bases of different strengths. This knowledge is very important in studying acid-base neutralisation reactions and in deciding the type of indicator to be used in such reactions.

Case I. Neutralisation reaction of strong acid and strong base : Such a reaction produces a salt which is not hydrolysed. For example HCl and NaOH produce NaCl and H_2O. NaCl is not reacted upon by H_2O. Thus the reaction is basically a pure H^+/OH^- reaction resulting in the formation of neutral water. The pH of the solution during the progress of a neutralisation of this type can be easily calculated on the basis of H^+ ion still remaining or on the basis of excess OH^- added. In practice it is observed that there is a sharp pH change (by about 6 pH units from pH 4 to pH 10) close to the equivalence point (Fig 8.2).

Case II. Neutralisation reaction of weak acid and strong base : A reaction between weak CH_3COOH and NaOH leads to the formation of CH_3COONa which is prone to hydrolysis. The pH of solutions during such titrations can be calculated with the help of the following equation :

$$\text{pH} = \tfrac{1}{2}pK_W + \tfrac{1}{2}pK_A + \tfrac{1}{2}\log C$$

At the equivalence point pH changes over a short range (pH 8 to pH 10) (Fig. 8.3).

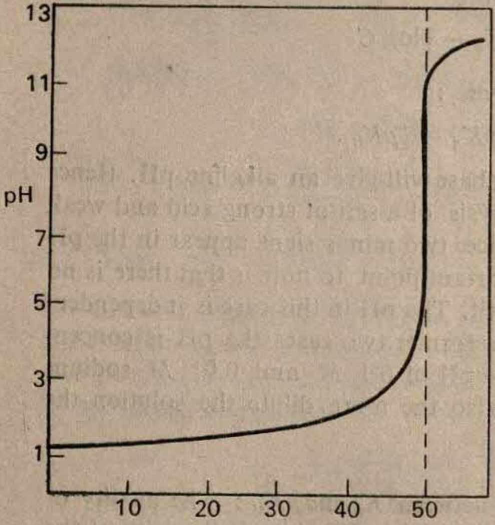


Fig.82. 50 ml of 0.1 N HCl is being titrated with 0.1 N NaOH

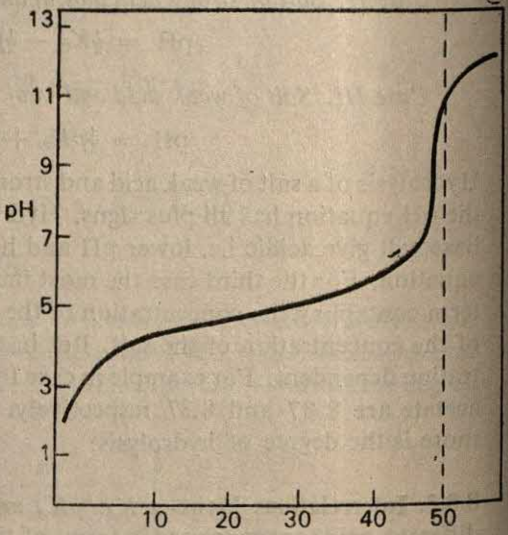


Fig.8.3 50 ml of 0.1 N CH_3COOH is being titrated with 0.1 N NaOH

Case III. Neutralisation reaction of a strong acid and a weak base : The salt produced in such titrations is hydrolysed to give acid reaction at the equivalence point. The pH of such a reaction can be calculated with the help of the following relation :

$$\text{pH} = \tfrac{1}{2}pK_W - \tfrac{1}{2}pK_B - \tfrac{1}{2}\log C$$

An example is the titration of NH_4OH with HCl. The salt NH_4Cl will get hydrolysed to give an acid reaction around the equivalence point. The pH changes from around 6 to 4 around the equivalence point.

Case IV. Neutralisation reaction of a weak acid and weak base : The pH changes can be calculated from the following relation :

$$pH = \tfrac{1}{2}pK_W + \tfrac{1}{2}pK_A - \tfrac{1}{2}pK_B$$

pH change during such a titration around the equivalence takes place close to 7.

8.10. CHOICE OF INDICATORS DURING ACID-BASE TITRATIONS

There are some organic dyes which produce two different colours in the un-ionised and ionised states. The dissociation of these dyes are therefore pH dependent. Some particular dyes change their colour in the pH range of acid – base titrations. Depending on the pH changes at the equivalence point of typical acid-base titrations (cf. Cases I to IV) it is possible to make the right choice of the organic dye to mark the end-point of the titration. Such dyes which allow us to mark the end points of acid-base titrations are known as *acid-base indicators.* To illustrate how this choice is made we will take the case of methyl orange (Fig. 8.4).

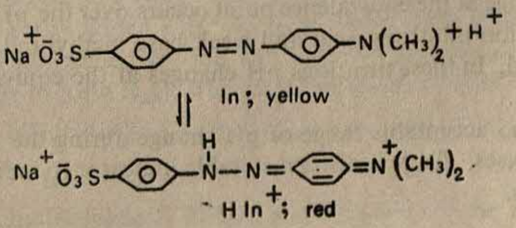


Fig. 8.4. The two forms of methyl orange.

Methyl orange (abbreviated HI_n^+) has a dissociation constant of the order of 10^{-4} (exact $pK_A = 3.7$). The colour in the un-dissociated and the dissociated forms are respectively red (HI_n^+) and yellow (I_n)

We can write the following relations :

$$\underset{\text{red}}{HI_n^+} \rightleftharpoons H^+ + \underset{\text{yellw}}{I_n} \; ; \quad K_A = \frac{[H^+]\,[I_n]}{[HI_n^+]} \simeq 10^{-4}$$

When the concentrations of HI_n^+ and I_n are equal $K_A \simeq 10^{-4} = [H^+]$.

At this point i.e. at pH $\simeq$ 4 the colour concentrations of the dissociated and the un-dissociated forms are equal. In other words around pH 4 the colour of methyl orange is in between red and orange. When the solution has a pH below 4 the acidic colour i.e. red colour will predominate while when the pH is above 4 the alkaline colour i.e. the yellow colour will appear. Thus we can profitably use methyl orange as an acid-base indicator in those titrations where the pH changes within the range 4 to 6 around the equivalence point. It is thus a suitable indicator in titrations of (a) strong acid and strong base and (b) strong acid and weak base. Phenolphthalein, a colourless organic dye in the undissociated form, changes its colour to beautiful pink at around pH 8.5 to 10. It is thus quite a suitable indicator in the titration of strong acid-strong base. (Table 8.4)

Table 8.4. Some Common Acid-Base Indicators

Indicator	pH range for colour change	Acidic color	Alkaline colour
Methyl orange	3.1 – 4.4	Red	Yellow
Methyl red	4.4 – 6.2	Red	Yellow
Litmus	4.5 – 8.3	Red	Blue
Bromothymol blue	6.0 – 7.6	Yellow	Blue
Phenolphthalein	8.5 – 10.0	Colourless	Pink

Remember the following guidelines :

1. For titration of strong acid and strong base any indicator can be used since the pH changes over a wide range (4 to 10) at the equivalence point.
2. For titration of weak acid and strong base phenolphthalein alone is suitable since the pH change at the equivalence point occurs over the pH range close to 10.
3. For titration of strong acid and weak base methyl red or methyl orange may be employed. In these titrations pH changes at the equivalence point are in the range 4 to 6.
4. There is no acceptable range of pH change during the titrations of weak acids and weak bases. There is also no suitable indicator to indicate the end point of such titrations.

8.11. BUFFER SOLUTIONS

We may begin this discussion by citing how mother nature has very cleverly manipulated our body system to resist large changes in pH. The blood that flows through the body system has a pH 7.4. But surprisingly even if enough acid is added to a litre of blood to make it 0.01 M in acid there is but a slight change in pH : 7.4 ± 0.1. Similar will be the case if the blood is treated with NaOH. Consider we carry this process out in pure water. We can perform very simple calculations to show that on making the water 0.01 M i.e. $10^{-2}M$ in acid the pH will change from neutral pH 7 to pH 2. In the case of NaOH, pOH will be 2 i.e. pH will be $14 - 2 = 12$. Blood functions as a buffer medium. *A buffer solution may be defined as one that resists large changes in pH on the addition of an acid or an alkali.*

What then is the origin of the buffer action? The buffer must contain compounds which can absorb the added H^+ ion or the OH^- ion. This will be possible only if the buffer contains a good conjugate acid-base pair. For example we conceive a solution made of sodium acetate and acetic acid. This system is composed of a weak acid and its salt. The salt will be fully dissociated to give acetate ions. These acetate ions will be good enough to take up the H^+ ions to form the weakly dissociated acetic acid. On the other hand any extra OH^- ions will be taken care of by the H^+ ions of the acetic acid :

$$\underset{\text{conjugate base}}{CH_3COO^-} + H^+ \longrightarrow \underset{\text{conjugate acid}}{CH_3COOH}$$

$$OH^- + \underset{\text{conjugate acid}}{CH_3COOH} \longrightarrow H_2O + \underset{\text{conjugate base}}{CH_3COO^-}$$

The pH of a buffer solution composed of a weak acid and a strong base can be computed by Henderson equation :

$$pH = pK_A + \log \frac{[Salt]}{[Acid]}$$

It can be easily seen that when the concentrations of the salt and the acid are the same the above relation reduces to :

$$pH = pK_A$$

Let us now take a look into the buffer solution made up of weak base and its salt. A common example may be found in NH_4Cl and NH_4OH. Ammonia being a weak base its conjugate acid NH_4^+ must be a strong one and hence will be quite efficient in trapping any added OH^- to form the weakly dissociated NH_4OH. On the other hand any added H^+ ion will link up the with slightly dissociated OH^- ion of NH_4OH to form H_2O. The reactions are as follows :

$$NH_4Cl \rightarrow NH_4^+ + Cl^- ; \; NH_4^+ + OH^- \rightarrow NH_4OH \text{ (weak base)}$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-; \; OH^- + H^+ \rightarrow H_2O$$

Thus we see that a buffer made of NH_4Cl and NH_4OH will be able to resist any large change of pH due to the addition of fresh acid or alkali. We can go for the calculation of the pH of such a buffer as described below :

$$MOH \rightleftharpoons M^+ + OH^-$$

$$K_B = \frac{[M^+][OH^-]}{[MOH]} = \frac{[M^+]}{[MOH]} \cdot \frac{K_W}{[H^+]} \text{ (since } K_W = [H^+][OH^-])$$

$$[H^+] = \frac{[M^+]}{[MOH]} \cdot \frac{K_W}{K_B}$$

$$\text{Therefore pH} = pK_W - pK_B - \log \frac{[M^+]}{[MOH]} = pK_W - pK_B - \log \frac{[Salt]}{[Base]}$$

When the concentrations of the acid and the base are equal the above relation simplifies to :

$$pH = pK_W - pK_B$$

We can arrive at the above relation by following a simpler route. Just as we have deduced a Henderson equation for the pH of a buffer solution we can write a similar parallel equation for pOH :

$$pOH = pK_B + \log \frac{[Salt]}{[Base]}$$

But $\mathrm{pH} + \mathrm{pOH} = pK_W$; therefore $pK_W - \mathrm{pH} = pK_B + \log \frac{[\mathrm{Salt}]}{[\mathrm{Base}]}$

Thus we have $\mathrm{pH} = pK_W - pK_B$ when [Salt] = [Base]

Now we would like to answer one last question : how do we go for selecting a buffer of desired pH? The answer lies in a proper appreciation of the Henderson equation. *The buffer of the desired pH must be prepared from an* (*a*) *acid-salt or* (*b*) *base-salt system such that the* pK_A *of the acid is as close to the desired pH.* This selection means we enforce the condition that [Salt]/[Acid] i.e. the ratio is close to unity. Thus maximum effectiveness against increase or decrease in pH is ensured. However the actual concentrations of acid and salt employed will be dictated by the desired resistance to change in pH. It can be guessed that the greater the concentrations of the acid and the conjugate base the greater will be the resistance of the buffer towards any change in pH on the addition of acid or base. The capacity of a buffer is a measure of the resistance to changes in pH. Quantitatively, *buffer capacity is defined as the number of moles of strong base required to change the pH of one litre of the solution by one pH unit.*

Table 8.5 records several common buffer systems with their pH range.

Table 8.5. Buffer solutions and pH Scales

Acid/Base and Salt	pH Range
Acetic acid and sodium acetate	3.7 — 5.6
Acetic acid and ammonium acetate	3.0 — 6.0
Ammonium chloride and ammonium hydroxide	8.5 — 10.0
Boric acid and borax	6.8 — 9.2
Disodium hydrogen phosphate (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4)	5.8 — 8.0

Problem 1 : A buffer solution is 0.1 *M* in acetic acid and 0.1 *M* in sodium acetate. Calculate its pH (given K_A of acetic acid $= 1.8 \times 10^{-5}$)

$$K_A = \frac{[\mathrm{H^+}]\,[\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]} = \frac{[\mathrm{H^+}]\ (0.1)}{0.1} = 8.1 \times 10^{-5}$$

$$[\mathrm{H^+}] = 1.8 \times 10^{-5} \ ; \quad \therefore \ \mathrm{pH} = -\log(1.8 \times 10^{-5})$$
$$= -(0.26 - 5.00) = 4.74$$

We can arrive at the pH value by taking recourse to Henderson equation as well.

$$\mathrm{pH} = pK_A + \log \frac{[\mathrm{Salt}]}{[\mathrm{Acid}]}$$

Since both the salt and the acid are of equal strength the relation simplifies to :

$$\mathrm{pH} = pK_A = -\log K_A = -\log(1.8 \times 10^{-5})$$
$$= -(0.26 - 5.00) = 4.74$$

Problem 2 : Sufficient HCl is added to a sodium acetate – acetic acid buffer so as to make the over-all concentrations of CH_3COOH, CH_3COONa and HCl 0.1 *N*, 0.1 *N* and 0.01 *N* respectively. Calculate the pH of the resulting solution (given K_A of acetic acid $= 1.8 \times 10^{-5}$)

Addition of 0.1 *N* HCl will reduce the concentration of the acetate ion from the original value of 0.1 *N* to (0.1 – 0.01 = 0.09 *N*). The concentration of the acetic acid will consequently go up to 0.1 + 0.01 = 0.11 *N*). Now we can employ Henderson equation :

$$\begin{aligned} pH &= pK_A + \log [CH_3COO^-]/[CH_3COOH] \\ &= -\log(1.8 \times 10^{-5}) + \log(0.09/0.11) \\ &= 4.74 - 0.08 = 4.66 \end{aligned}$$

The young reader is advised to solve the problem without using the Henderson equation. Find out the concentrations of the different species and make use of the K_A of acetic acid.

Problem 3 : We are required to prepare 500 ml of an acetic acid-sodium acetate buffer of pH 5.00. What should be the ratio of the two components? (K_A of acetic acid $= 1.8 \times 10^{-5}$).

We have to use the Henderson equation :

$$\begin{aligned} pH &= pK_A + \log [\text{Salt}]/[\text{Acid}] \\ 5.00 &= -\log(1.8 \times 10^{-5}) + \log [\text{Salt}]/[\text{Acid}] \\ &= 4.74 + \log [\text{Salt}]/[\text{Acid}] \end{aligned}$$

Therefore $\log [\text{Salt}]/[\text{Acid}] = 5.00 - 4.74 = 0.26$

$\therefore$ $[\text{Salt}]/[\text{Acid}] = \text{antilog of } 0.26 = 1.82$

This means the desired buffer solution of pH 5.00 should have 1 mole of acetic acid and 1.8 moles of sodium acetate per litre of the solution. Hence for 500 ml. of the buffer solution we should use 0.5 mole of acetic acid and 0.9 mole of sodium acetate.

8.12. EQUIVALENT WEIGHTS OF ACIDS AND BASES

8.12.1. Basicity of an acid and acidity of a base : A hydrogen containing acid has certain number of replaceable hydrogen ions. Similarly a hydroxide containing base has certain number of replaceable OH-ions. Acid-base neutralisation in aqueous medium really means reaction between H^+ ions and OH^- ions to give neutral H_2O. *Basicity of an acid may be defined classically as the number of* OH^- *ions with which it can react*. For example H_2SO_4 can react or neutralise two OH^- ions ; hence the basicity of H_2SO_4 is two. HNO_3, HCl, $HClO_4$ acids have a basicity of one i.e. these are *monobasic acids*. H_2SO_4, H_2SeO_4, H_2SO_3 are *dibasic acids*. H_3PO_4, H_3BO_3 are *tribasic acids*.

Bases usually possess OH^- ions. Each such OH^- ion can react with one H^+ ion. So *acidity of a base may be defined as the number of* H^+ *ions with which it can* *react*. Those bases containing only one OH^- ion are *monoacidic base* while those containing two OH^- ions are *diacidic base* and so on. Common examples of monoacidic bases are NaOH, KOH, $(CH_3)_4NOH$, NH_4OH etc. $Ca(OH)_2$, $Mg(OH)_2$, $Ba(OH)_2$ etc. are diacidic bases while $Al(OH)_3$, $La(OH)_3$, etc. afford examples of *triacidic bases*.

8.12.2. Equivalent weights : *Equivalent weight of an acid is that weight which corresponds to one gram atom of hydrogen i.e. to* 1.0078 *gram of hydrogen*. It immediately follows that for monobasic acids the equivalent weight is the molecular weight. For dibasic and tribasic acids the equivalent weights are respectively half and one-third of the respective molecular weights.

Equivalent weight of a base is that weight which corresponds to one gram ion of OH^- i.e. to 17.0078 *gram*. We can easily guess that the equivalent weights of monoacidic, diacidic and triacidic bases are one gram molecular weight, half gram molecular weight and one-third gram molecular weights of the respective bases. Thus the equivalent weight of $Mg(OH)_2$ is half its gram molecular weight. The equivalent weight of $La(OH)_3$ will be one-third of the molecular weight.

8.12.3. Equivalent weights of acids and bases are not invariant : Since monobasic acids have just one replaceable hydrogen atom it follows that they can but show only one equivalent weight—which is the same as their molecular weights. But when we come to *polyprotic acids* i.e. *polybasic acids* their response to neutralisation will be dictated by their two or more acid dissociation constants. Equivalent weights will be decided by the extent of acid-base reaction carried out. *As a matter of fact such acids are the ones that give normal* and *acid salts*. We will cite two examples to clarify the point.

Case I. The case of sodium carbonate and carbonic acid : H_2CO_3 is a weak dibasic acid and naturally has two dissociation constants :

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \; ; K_{A_I} = 4.3\times10^{-7} \; ; pK_{A_I} = 6.4$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \; ; K_{A_{II}} = 5.6\times10^{-11} \; ; pK_{A_{II}} = 10.25$$

When we prepare a standard solution of Na_2CO_3 and go on titrating this solution by a standard acid solution a stage will come when an equimolar proportion of $NaHCO_3$ will be produced in solution :

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

The pH at this stage can be calculated approximately by the use of the appropriate equation. Let us assume we start with 100 ml. of 0.1 *M* of Na_2CO_3 and add 100 ml. of 0.1 *M* HCl, then the concentration of the salt $NaHCO_3$ produced will be 0.05 *M*. Therefore the pH of the solution at that stage will be given by .

$$\begin{aligned} pH &= \tfrac{1}{2}pK_W + \tfrac{1}{2}pK_{A_I} + \tfrac{1}{2}\log C \\ &= \tfrac{1}{2}(14) + \tfrac{1}{2}(6.4) + \tfrac{1}{2}\log(0.05) = 9.55 \end{aligned}$$

There is another way of calculating such pH for polybasic acid neutralisation which we will not deduce but will simply put down as :

$$\mathrm{pH} = \tfrac{1}{2}pK_{A_I} + \tfrac{1}{2}pK_{A_{II}} = \tfrac{1}{2}(6.4) + \tfrac{1}{2}(10.25) = 8.32$$

In any case it can be appreciated even without going into these calculations that at the stage of the formation of the salt $NaHCO_3$ the solution will give an alkaline pH as $NaHCO_3$ is a salt of a strong base and weak acid. We thus can follow this stage of neutralisation by using phenolphthalein as the indicator.

The second stage of the neutralisation will produce H_2CO_3 and NaCl :

$$Na_2CO_3 + 2HCl \rightarrow H_2CO_3 + 2NaCl$$

The sodium chloride being a salt of a strong acid and a strong base will not influence the pH of the medium. We have therefore to calculate the pH of the solution by taking into consideration the dissociation of the carbonic acid. Since the second dissociation is very weak we can easily neglect that :

$$K_{A_I} = \frac{[H^+]\ [HCO_3^-]}{[H_2CO_3]} = \frac{[H^+]^2}{[HCO_3]} = 4.3 \times 10^{-7}$$

Assuming that we have been operating with a 0.1 *M* solution the $[H^+]$ and pH will be as worked out below :

$$[H^+] = \sqrt{4.3 \times 10^{-7} \times 0.1} \simeq 2 \times 10^{-4}\ ;\ \mathrm{pH} = 3.7$$

We can now see that the pH at this second equivalence point is within the range where methyl orange changes colour. So titre value of the HCl solution will be twice as large when methyl orange is used compared to that with phenolphthalein.

The final conclusion is that equivalent weight of Na_2CO_3 or for that matter of H_2CO_3 is its molecular weight when phenolphthalein is used as the acid-base indicator. On the other hand the equivalent weight is half the molecular weight when we use methyl orange. Thus we see that the equivalent weight of Na_2CO_3 is not an invariant quantity.

Case II : The case of orthophosphoric acid : Orthophosphoric acid is a tribasic acid with the following values of the three dissociation constants :

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \quad ; \quad K_{A_I} = 7.5\times10^{-3}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \quad ; \quad K_{A_{II}} = 6.2\times10^{-8}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \quad ; \quad K_{A_{III}} = 5.0\times10^{-13}$$

The first step neutralisation of H_3PO_4 by a standard solution of alkali can be detected around pH 4.6 with the help of methyl orange or methyl red while the second point can be identified around pH 9.7 with phenolphthalein. Thus if we consider the first step only the equivalent weight becomes the same as the molecular weight. On the contrary the second stage of neutralisation gives the equivalent weight as half the molecular weight. The third equivalence point cannot be followed easily because the change of pH is very gradual and no suitable indicator is available.

EXERCISES

1. Write a connected account of Arrhenius, Bronsted-Lowry and Lewis' theories of acids and bases.

2. Explain with examples the terms : conjugate acid and conjugate base. Name the conjugate acids and bases of the following :

$$CH_3COOH\ ;\ CH_3COO^-\ ;\ H_2O\ ;\ NH_4OH\ ;\ NH_4^+\ ;\ HCl\ ;\ HSO_4^-\ ;\ N_3^-$$

3. What is meant by pH? How does it help us in expressing the acidity or alkalinity of a solution? How the pH changes with change in acid concentration of a solution?

4. Show that NH_3 is a base both by the definitions of Bronsted and Lewis. But BF_3 is a Lewis' acid but not an acid by Bronsted definition.

5. Indicate the Bronsted acids and bases in the following equilibria :

$$(a)\quad HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

$$(b)\quad CH_3COO^- + HCl \rightleftharpoons CH_3COOH + Cl^-$$

6. The pH of a solution of 105 gram HN_3 in a litre is 2.2. Calculate the dissociation constant of hydrazoic acid (answer : 1.6×10^{-5}).

7. Name two important acid-base indicators and discuss the types of neutralisation reactions in which you will use these indicators.

8. In a titration of a sodium carbonate solution what indicator would you use in identifying the end point?

9. What is a buffer solution? Explain with a few examples.

10. Write notes on :

(*a*) hydrolysis (*b*) Henderson equation (*c*) acid dissociation constant (*d*) acid and base character of water.

CHAPTER 9

SOLUTE, SOLVENT AND SOLUTION

9.1. INTRODUCTION

It is a common experience that some substances dissolve in particular solvents while many others do not. Thus common salt NaCl is easily soluble in water while the same NaCl is insoluble in common organic solvents. Again CCl_4 or C_6H_6 is insoluble in water but is readily soluble in organic solvents. A solution is the result of the dissolution of a solute in a solvent. This means that there should be a right combination of the solute and the solvent in order that a solution is produced. The question of solubility is a vexed problem and as yet it has not been possible to provide satisfactory answers to all questions related to solubility. However some general concepts on the role of the solute and the solvent have been developed. However these have to be accepted quite sportingly because these concepts are not all-proof. There will be many cases which will defy the accepted concepts and will agitate the minds of the young readers. Below we describe the two major explanations of solubility.

9.2. SOLUBILITY OF IONIC COMPOUNDS

In Chapter 5 we have seen that there are two broad classes of compounds : (a) ionic and (b) covalent. The ionic compounds consist of oppositely charged ions. Each one of these charged ions has its charge spherically distributed all over. Consequently a cation tends to drag as many of the oppositely charged ions i.e. anions around itself as possible. So also will be the case with the anion. The over-all result is that in an ionic compound we do not find discrete molecules but an assemblage of cations and anions to give rise to giant molecules. Thus our NaCl is just not a molecule consisting of one Na^+ and a Cl^- ion but the ionic crystal lattice is so arranged that each Na^+ ion is surrounded by as many as six Cl^- ions in a regular octahedral geometry and vice versa. As against this in covalent molecules no ions exist but electrons are shared between neighbouring atoms. Thus there is not much of an attractive force outside a particular molecule. Molecules are held together by weak van der Waals' force (Chapter 5). Thus in covalent molecules discrete molecules exist. It is in this backdrop that we have to search an answer to the problem of solubility.

When does an ionic compound dissolve in a solvent? The answer is that an ionic compound will dissolve in a particular solvent only if the solvent is powerful enough to reduce the electrostatic force of attraction between the oppositely charged ions. This again is possible when the solvent succeeds in increasing the distance between the cations and the anions. Let us consider two ions with charges q^+ and q^- separated by a distance r. Then according to Coulomb's law we have :

$$F \propto \frac{q^+ q^-}{r^2}; \quad F = \frac{1}{D} \cdot \frac{q^+ q^-}{r^2}$$

In the above relations F stands for the force while D is the proportionality constant, commonly called *dielectric constant*. From the above relation it follows that a large value of D will surely reduce the interionic force. Of the commonly used solvents dielectric constant of water is very high, namely 78.5. Therefore it is an ideal solvent for many ionic compounds like NaCl, KCl, $MgCl_2$, $CaCl_2$ etc. Even without going into the idea of dielectric constant we can present a graphic and qualitative picture of the above dissolution from an appreciation of the structure of H_2O. Although water is basically a covalent compound it is polar because of a substantial difference in the electronegativities of hydrogen (2.1) and oxygen (3.5). As a result the hydrogen end becomes positive with a fractional charge δ^+ while the oxygen end becomes negative with $\delta^- \delta^-$. The hydrogen ends will tend to attract the anion while the oxygen end will drag the cation. As a result the electrostatic force of attraction will decrease and the distance between the cation and the anion will increase. The final outcome will be the dissolution of the ionic compound in water. The usual covalent compounds like CCl_4 or $CHCl_3$ or C_6H_6 are devoid of ions and hence the mechanism by which they will be dragged into the polar solvent like water is non-existent. Hence dissolution in polar solvents is not possible. Again since organic solvents are usually non-polar they do not possess the right mechanism by which they can weaken the inter-ionic attraction of ionic compounds. Hence ionic compounds are as a rule insoluble in non-polar solvents.

9.3. SOLUBILITY OF COVALENT COMPOUNDS

We have already mentioned in the preceding section that covalent compounds are composed of non-ionic discrete molecules held together by weak van der Waals' force. Hence polar solvents are no good for dissolution of such compounds because these compounds do not possess ions which could be attracted by the oppositely charged polar ends of polar solvent molecules. However non-polar solvents possess the same kind of bonds as is found in the covalent compounds. These solvent molecules too are held together by the weak van der Waals' forces. Hence covalent solutes and covalent non-polar solvents find them alike so far as the bonding forces are concerned and hence do not mind interchanging positions. The sum-total effect is what the organic chemists usually call 'like dissolves like'.

9.4. ARE THESE MODELS OF SOLUBILITY ENOUGH

We have already cautioned the readers that we do not possess till today the background to explain the solubility in entirity. We have but given a qualitative approach based on the bonding patterns of the solute and the solvent. This is the approach inorganic chemists are fond of. But if you call upon a physical chemist to deliver a talk on solubility he will surely bring in very many energy terms like free-energy change, enthalpy, entropy, lattice energy and so on. As you can see the area is real complicated. The above approach given in terms of the nature of bonding will go a long way to explain many solubilities but not all. For example we are at a loss to explain why $BaSO_4$ is not soluble in water but the very sweet (but very dear indeed !) sugar is so very soluble.

Below we give the solubilities of some common inorganic salts :

1. The alkali metal salts and ammonium salts are in general soluble in water.

2. All nitrates and perchlorates (except $KClO_4$ and NH_4ClO_4) are soluble in water.

3. Sulphates of Sr^{2+}, Ba^{2+}, Ra^{2+} and Pb^{2+} are insoluble. Other sulphates are generally soluble.

4. Halides of Ag^+, Hg_2^{2+}, and Pb^{2+} are insoluble. Fluorides of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} are insoluble. Rest of the halides are soluble.

5. Oxides, hydroxides, carbonates and phosphates of the alkali metals and ammonium ion are soluble. All others are insoluble.

6. Alkali metal and ammonium sulphides are soluble. All other sulphides are insoluble.

Solubilities of the above inorganic compounds are made use of in devising a scheme for their qualitative detection in a mixture. Solubility of sparingly soluble salts in aqueous medium and in the presence of some ion common to both the sparingly soluble salt and the added salt plays a great role in the qualitative scheme of analysis. We therefore logically pass on to get an idea about the solubility of the sparingly soluble salts.

9.5. SPARINGLY SOLUBLE SALTS : SOLUBILITY PRODUCT

Silver chloride is a well-known sparingly soluble salt. If we take a good amount of AgCl and equilibrate this in water to get a saturated solution (1 litre) we will observe that a large amount will still remain insoluble. We can filter off the excess AgCl and then determine the concentration of the silver ion and the chloride ion. Such determination shows that 1.6×10^{-5} mole of AgCl dissolves per litre of the solution. Since the solution is quite dilute it is justified to assume that AgCl does dissociate completely into Ag^+ and Cl^- ions. We write the following equilibrium equation :

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \ (aq = \text{aqueous})$$

Following the generally accepted procedure of writing equilibrium constants we get :

$$K = \frac{[Ag^+]\,[Cl^-]}{[AgCl\,(s)]}$$

At equilibrium the concentration of a pure solid in the solid itself remains a constant. We can therefore cross multiply K by AgCl(s) to get another constant K_{sp} :

$$K_{sp} = K \times [AgCl(s)] = [Ag^+]\ [Cl^-]$$

Thus the new equilibrium constant K_{sp} is the product of the concentrations of the two ions in a saturated solution. This constant for a solubility equilibrium is called the *solubility product constant* or simply the *solubility product*. *Solubility product may be defined as the product of the concentrations of the ions each raised to the appropriate powers equal to the coefficients with which they appear in the solubility equation*. Take for example the case of sparingly soluble BaF_2. We have the following equations :

$$BaF_2(s) \rightleftharpoons Ba^{2+} + 2F^-$$

$$K = \frac{[Ba^{2+}]\ [F^-]^2}{[BaF_2(s)]} \quad ; \quad K_{sp} = [Ba^{2+}]\ [F^-]^2$$

Similarly the K_{sp} values of Ag_2CrO_4 and $Al(OH)_3$ are given by :

$$Ag_2CrO_4 \quad : \quad K_{sp} = [Ag^+]^2\ [CrO_4]$$

$$Al(OH)_3 \quad : \quad K_{sp} = [Al^{3+}]\ [OH^-]^3$$

For the benefit of the young learners we would like to point out that *the concentration of the solid reactant does not appear in the equilibrium constant expression*. This happens because of the constancy of the concentration of the sparingly soluble substance in the condensed solid state. Another way of expressing the same truth is to say that we have included the constant concentration of the pure sparingly soluble salt in the final equilibrium constant K_{sp}. Table 9.1 records the K_{sp} values of some sparingly soluble salts.

Table 9.1. Solubility Products of Sparingly Soluble Salts

Anion	Salt	K_{sp}	Anion	Hydroxide/Salt	K_{sp}
Acetate	$AgCH_3COO$	2×10^{-3}	Hydroxide	$Al(OH)_3$	5×10^{-33}
Bromide	$AgBr$	1×10^{-13}		$Cr(OH)_3$	1×10^{-30}
	$PbBr_2$	5×10^{-6}		$Fe(OH)_3$	5×10^{-38}
	$CuBr$	5.9×10^{-9}	Iodide	AgI	1×10^{-16}
Carbonate	$MgCO_3$	2×10^{-8}		PbI_2	1×10^{-8}
	$CaCO_3$	5×10^{-9}	Sulphate	$CaSO_4$	3×10^{-5}
	$BaCO_3$	1×10^{-9}		$SrSO_4$	7.6×10^{-7}
	$PbCO_3$	1×10^{-13}		$BaSO_4$	1.5×10^{-9}
				$PbSO_4$	1.8×10^{-8}
Chloride	$AgCl$	1.6×10^{-10}	Sulphide	Ag_2S	1×10^{-49}
	$PbCl_2$	1.7×10^{-5}		CdS	1×10^{-26}
	Hg_2Cl_2	1×10^{-18}		PbS	1×10^{-27}
				ZnS	1×10^{-23}
				CoS	1×10^{-21}
				HgS	1×10^{-52}

We can draw a general conclusion from Table 9.1. The lower the solubility product the more insoluble the compound is. Thus silver acetate appears to be the least insoluble ($K_{sp} \simeq 2\times10^{-3}$) while mercuric sulphide is the most insoluble ($K_{sp} \simeq 1\times10^{-52}$).

9.6. COMMON ION EFFECT

Let us prepare a saturated aqueous solution of AgCl and filter off the excess isoluble AgCl. We divide the clear solution of AgCl in two portions. In one portion we add a little solution of $AgNO_3$ while in the other we add a solution of NaCl. We will observe that in both the solutions turbidity appears and eventually a precipitate of AgCl forms. What does really happen to the solutions?

Addition of $AgNO_3$ to the clear solution of AgCl means we are adding an ion, namely Ag^+, which is common to both AgCl and $AgNO_3$. How does this addition affect the equilibrium of AgCl? The answer is found in an appreciation of the famous Le Chatelier principle. *The principle states that whenever an external constraint is imposed on a system at equilibrium the system will so react as to minimise the imposed constraint.* Addition of fresh silver ion to AgCl at equilibrium means we have, for the time being, more Ag^+ ions in solution than is permitted by the equilibrium constant of AgCl. Since this equilibrium constant is a characteristic of AgCl and is a constant, the system will so respond that the concentration of Ag^+ ion is reduced. This is possible when some Ag^+ ions combine with the chloride ions in solution to precipitate out as the insoluble AgCl. Effectively there will be a lowering of the chloride ion concentration and the original equilibrium constant of AgCl will be maintained. Now let us see what would occur on the addition of NaCl. This time the chloride ion is common to both AgCl and NaCl. Once again, for the time being, there will be many more chloride ions in solution than can be allowed by the equilibrium constant of AgCl. The system will therefore so respond that the effect of additional Cl^- ions can be negated. This will be realised when some of the chloride ions combine with some Ag^+ ions to form the insoluble AgCl. In essence there will be a reduction of the silver ions in the solution and the original equilibrium constant i.e. the solubility product will be retained. *Common ion effect may be defined as the effect that is brought about on the equilibrium of weakly dissociated salt or a sparingly soluble salt by an electrolyte having an ion common to itself as well as the other compound.*

We have introduced the common ion effect by invoking the example of how the solubility of AgCl is influenced by the addition of $AgNO_3$ or NaCl. A very fine example of common usage is how addition of NH_4Cl to the weakly dissociated base NH_4OH regulates the precipitation of the hydroxides of iron (III), aluminium (III) chromium (III) etc. While these three hydroxides are precipitated those of cobalt (II), nickel (II), zinc (II) manganese (II) are not. While the first three hydroxides have appreciably low solubility products those of the other metal ions are rather high : K_{sp} : $Al(OH)_3$, 5×10^{-33} ; $Zn(OH)_2$, 5×10^{-17}. A *precipitate of a sparingly soluble compound appears when the concentration product in aqueous medium exceeds the corresponding solubility product.* NH_4OH is a weak base and when present alone in solution will be able enough to bring down the precipitates of the hydroxides of zinc (II), nickel(II), cobalt(II) and manganese (II). In order to avoid the precipitation we have to create a situation so that the solubility products of these hydroxides cannot be exceeded in solution. This can be achieved if the available concentration of OH^- ions through the dissociation of NH_4OH can be substantially reduced. Just this situation is realised by the addition of the salt NH_4Cl. Now once again we have to make use of the principle enunciated by Le Chatelier. The equilibrium of the weakly dissociated NH_4OH will be influenced on the addition of the completely dissociated salt NH_4Cl. The common ion NH_4^+ will be in very large excess than is permitted by the equilibrium constant of NH_4OH. As a result the system will so react that concentration of NH_4^+ ions in solution is reduced. This is achieved by the combination of good many NH_4^+ ions with OH^- ions to produce undissociated NH_4OH molecules. Thus in effect the solution has less number of OH^- ions in the presence of NH_4^+ ions than in its absence i.e. NH_4OH is rendered a still weaker base in the presence of NH_4Cl. Hence the solubility products of the hydroxides of zinc (II) etc. are not exceeded and the ions are still retained in solution. The following problem will make things quantitatively clear.

Problem 1 : 0.25 gram mole of NH_4Cl is dissolved in a litre of 0.1 M NH_4OH. To what degree the dissociation of NH_4OH will be influenced ? ($K_B = 1.8\times10^{-5}$)

Let us assume that the degree (i.e. fraction) of dissociation of 0.1 M NH_4OH be α. Concentration of the NH_4OH is $c = 0.1\ M$. We can write the following relation to express K_B of NH_4OH :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- ;\quad K_B = \frac{[NH_4^+]\ [OH^-]}{[NH_4OH]} = \frac{\alpha.c.\alpha.c}{(1-\alpha)c}$$

$$= \frac{\alpha^2 c}{1-\alpha}$$

Since NH_4OH is a weak base the degree of dissociation must be really small compared to 1. Hence the above relation reduces to :

$$K_B = \alpha^2 c = \alpha^2\times 0.1 = 1.8\times10^{-5}$$

Therefore $\quad \alpha = \sqrt{(1.8\times10^{-5})/0.1} = 0.0135$

The OH^- concentration $= [NH_4^+] =$ degree of dissociation × concentration

$$= 0.0135\times0.1 = 1.35\times10^{-3}$$

Concentration of undissociated $NH_4OH = [NH_4OH] = 0.1 - 0.00135 = 0.0986M$. In the presence of added NH_4Cl the degree of dissociation will be lowered. Let this new degree of dissociation be α'. Then we have :

$$[OH^-] = \alpha'.c = 0.1\,\alpha';\ \text{undissociated } [NH_4OH] = (1-\alpha').c. = c = 0.1\ M.$$

We have to appreciate that NH_4Cl is fully dissociated and in the presence of NH_4Cl the dissociation of NH_4OH will be further supperssed. But K_B has to be maintained constant. This can be achieved only if the NH_4^+ ions react to an appreciable extent with the OH^- ions to produce more of undissociated NH_4OH. Thus we have :

$$K_B = \frac{[NH_4^+]\ [OH^-]}{[NH_4OH]} = \frac{\times 0}{1} = 1.8\times10^{-5}$$

Therefore $\alpha' = 7.2\times10^{-5}$; $[OH^-] = 0.1\alpha' = 7.2\times10^{-6}$

Thus the final result is this: the original concentration of OH^- in aqueous NH_4OH was 1.35×10^{-3} while that in the presence of $0.25M$ NH_4Cl is 7.2×10^{-6}. Thus NH_4OH—normally a weak base—is rendered weaker still in the presence of a common ion salt NH_4Cl.

9.7. SOME PROBLEMS ON SOLUBILITY PRODUCT

Problem 1 : The barium ion concentration in a saturated BaF_2 aqueous solution is 7.6×10^{-3} mole per litre. Calculate the solubility product of BaF_2 and also the concentration of the fluoride ion.

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^- \; ; \; K_{sp} = [Ba^{2+}]\,[F^-]^2$$

For every mole of BaF_2 there will be two moles of fluoride ion. Let us take x as the molar concentration of BaF_2 in the saturated aqueous solution. Then the concentration of the fluoride ion will be $2x$. Then :

$$K_{sp} = x\times(2x)^2 = 4x^3 = 4\times(7.6\times10^{-3})^3 = 1.7\times10^{-6}$$

concentration of the fluoride ion $2x = 2\times7.6\times10^{-3} = 15.2\times10^{-3}M$

Problem 2 : Solubility product of BaF_2 is 1.7×10^{-6}. Calculate the solubility of BaF_2 in (a) saturated aqueous solution and (*b*) in $0.1M$ sodium fluoride.

(*a*) If we take x as the solubility of BaF_2 then the concentrations of the barium ion and the fluoride ion are x and $2x$ respectively. So the K_{sp} will be $x\times(2x)^2=4x^3$..

$$K_{sp} = 4x^3 = 1.7 \times 10^{-6} \; ; \quad x^3 = 0.4 \times 10^{-6}$$

$$x = 7.6 \times 10^{-3} \text{ mole/litre}$$

(*b*) If the concentration of the dissolved BaF_2 is x then the concentration of fluoride ion will be $2x$. But compared to the large concentration of the fluoride ion coming from 0.1 M NaF it must be low enough. Hence this can be safely neglected.

$$K_{sp} = x\times(0.1)^2 = x\times10^{-2} = 1.7\times10^{-6}$$

Therefore $x = 1.7\times10^{-4}$ mole/litre

Problem 3 : To a solution of $0.1M$ $BaCl_2$ sodium sulphate solution is being added. At what sulphate ion concentration first precipitation should start ? ($K_{sp} = 1.1 \times 10^{-10}$).

Precipitation of $BaSO_4$ will begin when the concentration product of the two ions i.e. of Ba^{2+} and SO_4^{2-} in solution will exceed that of the solubility product of $BaSO_4$.

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

Therefore $K_{sp} = [Ba^{2+}]\,[SO_4^{2-}] = 1.1\times10^{-10}$

Sulphate ion concentration $= (1.1\times10^{-10})/0.1 = 1,1\times10^{-9}\ M$

Precipitation will start when the concentration of sulphate ion exceeds $1.1 \times 10^{-9} M$.

Problem 4 : Chromate ion is added to a 0.01 *M* $AgNO_3$ solution such that the concentration of chromate ion becomes $2 \times 10^{-3} M$. Calculate the concentration of Ag^+ ion in solution under equilibrium condition and find out what percentage of silver ion will be retained in solution. (K_{sp} of Ag_2CrO_4 : 1×10^{-12})

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-} \; ; \; K_{sp} = [Ag^+]^2 [CrO_4^{2-}] = 1 \times 10^{-12}$$

$$\text{Therefore } [Ag^+]^2 = (1 \times 10^{-12})/(2 \times 10^{-3}) = 5 \times 10^{-10}$$

$$[Ag^+] = \sqrt{5 \times 10^{-10}} \simeq 2 \times 10^{-5} M$$

Under equilibrium condition the concentration of silver ion that will be retained after combining with the added chromate ion is therefore $\simeq 2 \times 10^{-5} M$.

$$\text{Percentage of } Ag^+ \text{ being retained} = \frac{\text{equilibrium concentration}}{\text{original concentration}} \times 100$$

$$= 0.2\%$$

$$\text{Therefore silver ion precipitated} = 100 - 0.2 = 99.8\%$$

Problem 5 : Solubility product of $PbBr_2$ is 5×10^{-6}. Calculate its solubility in gram/litre (atomic weight of Pb and Br are 207 and 80).

$$PbBr_2 \rightleftharpoons Pb^{2+} + 2Br^- \; ; \; K_{sp} = [Pb^{2+}] \, [Br^-]^2$$

If x is the concentration of Pb^{2+} ion then the concentration of the bromide ion will be $2x$. Therefore we have :

$$K_{sp} = x \times (2x)^2 = 4x^3 = 5 \times 10^{-6}$$

$$\begin{aligned} \text{Therefore } x &= 1.08 \times 10^{-2} \text{ gram mole/litre} \\ &= 1.08 \times 10^{-2} \times \text{molecular weight/litre} \\ &= 1.08 \times 10^{-2} \times 367 \text{ gram/litre} \\ &= 3.96 \text{ gram/litre} \end{aligned}$$

It is hardly necessary to repeat that the concentration of Pb^{2+} ion is the same as the concentration of $PbBr_2$.

9.8. APPLICATIONS OF SOLUBILITY PRODUCT PRINCIPLE IN QUALITATIVE ANALYSIS

In a later Chapter we will devote some space for qualitative analysis of metal ions and some anions. The separation of many of the metal ions in the qualitative scheme is dependent, to a large extent, on the solubility product principles.

1. *Separation of Group I metal ions* : The group I comprises the ions Ag^+, Pb^{2+} and Hg_2^{2+}. On the addition of dilute HC*l* to an aqueous solution of the basic

radicals these three ions are precipitated as their sparingly soluble chloride salts AgCl, $PbCl_2$ and Hg_2Cl_2. The K_{sp} values of these three chlorides are 1.6×10^{-10}, 1.7×10^{-5} and 1.0×10^{-18}. The values tell us that whereas the chlorides of silver (I) and mercury (I) are pretty insoluble that of lead (II) has some solubility. This explains why the entire amount of lead (II) is not always precipitated. A portion of it is often carried into the second group of the qualitative scheme where it is precipitated as PbS along with the other sulphides.

2. *Selected precipitation of metal sulphides* : A large number of metal ions are precipitated as their sulphides depending on the pH of the medium. The sulphides of copper (II), cadmium (II), mercury (II), arsenic (III) antimony (III), bismuth (III) and tin (II) are highly insoluble i.e. their solubility product values are very low. Compared to this group of metal sulphides there is another group of metals like cobalt (II), zinc (II), nickel (II) and manganese (II) whose sulphides have *comparatively* larger values of their K_{sp} .

	K_{sp}		K_{sp}
CuS	1×10^{-45}	CoS	1×10^{-21}
HgS	1×10^{-52}	MnS	1×10^{-13}
CdS	1×10^{-26}	NiS	1×10^{-22}

It is quite evident that only a small amount of sulphide ion in solution will be sufficient to exceed the K_{sp} values of the sulphides of the first group of metal ions. But to precipitate the second group of metal ions we need to increase the concentration of the sulphide ions in solution. In acid medium due to the presence of the common H^+ ion we get little of sulphide ion (S^{2-}) but in alkaline medium the concentration of S^{2-} is quite appreciable. Calculations based on the K_{AI} ($\sim 10^{-7}$) and K_{AII} ($\sim 10^{-15}$) of H_2S show that in 0.2 to 0.3 N HCl solution saturated with H_2S the sulphide ion ($[S^{2-}]$) concentration is sufficient to exceed the K_{sp} values of HgS, CuS etc. while it is too low to exceed the K_{sp} values of CoS, ZnS, NiS etc. Hence HgS, CuS etc. are precipitated by H_2S in dilute HCl medium but CoS, NiS, ZnS are not. In ammoniacal medium, however, the sulphide ion concentration is high enough to exceed the K_{sp} values of CoS, ZnS etc. Hence these sulphides are precipitated by passing H_2S through an NH_4Cl-NH_4OH solution.

3. *Precipitation of the hydroxides of Fe^{3+}, Al^{3+} Cr^{3+} and the sulphides of Co^{2+}, Ni^{2+}, Zn^{2+}* and *Mn^{2+}* : Although NH_4OH is a weak base the OH^- ions available through its dissociation in aqueous medium are sufficient to exceed the solubility products of the hydroxides of all these metal ions. But in the presence of the salt NH_4Cl, with a common ion, its dissociation is arrested to a significant extent to make it a far weaker base. The available OH^- ion concentration in the presence of NH_4Cl is enough to exceed the K_{sp} values of Fe^{3+}, $Al^{3+}$and Cr^{3+} but not of the others. Hence there is a selective precipitation of the three hydroxides. The other metal ions (Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}) are retained in solution and later precipitated by bubbling in H_2S and precipitating as the sulphides. This is the background of separation of the two sub-groups IIIA (Fe^{3+}, Al^{3+} and Cr^{3+}) and IIIB (Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}).

EXERCISES

1. Discuss how the solubilities of ionic and covalent compounds are influenced by the polarity of the solvent.

2. What is dielectric constant? Dielectric constants of water and liquid ammonia are 78.5 and 22 respectively. Which is a better solvent for ionic compounds?

3. Point out which of the following compounds will be easily soluble in water :

$NaCl$, CCl_4, KBr, KI, $CHCl_3$, C_6H_6

4. What do you understand by solubility product? Arrange the following compounds in order of increasing solubility in water. The respective solubility products are given for the purpose :

$AgBr$, 1×10^{-13}, PbI_2, 1×10^{-8}, HgS, 1×10^{-52}, $AgCH_3COO$, 2×10^{-3}

5. What is common ion effect? Discuss how this concept has helped us in developing suitable methods of separation of metal ions for their qualitative detection.

6. Write a concise account of how solubility product principle has worked in the development of the qualitative scheme of analysis of metal ions.

CHAPTER 10

ALLOTROPY, POLYMORPHISM, ISOMORPHISM AND ISOMERISM

In order to appreciate some aspects of descriptive inorganic chemistry we have to get familiar with some very closely related terms. These are allotropy, polymorphism, isomorphism and isomerism. Of these terms allotropy refers to elementary states and the rest to compounds. The term 'isotope' also refers to elementary states and specifically to atoms. We will have a final section to highlight the difference between allotropes and isotopes.

10.1. ALLOTROPY

Quite a few elements are known to exist in more than one form in the same physical state. These different forms are called allotropes or allotropic modifications of the element. The phenomenon by virtue of which an element gives rise to the allotropes is called allotropy.

The elements which generally show allotropy are oxygen, sulphur, carbon and phosphorus. The question that we now need to answer is : what is the reason that the same very element of the periodic table exists in more than one form in the same physical state? There are two reasons that may lead to allotropy : (*a*) Molecules of the element concerned may have different number of atoms and (*b*) Molecules of the element may possess different crystal structures. We know that the element oxygen exists in the same gaseous state in two forms—*oxygen* and *ozone*. While oxygen molecules are diatomic, ozone molecules are triatomic. Allotropy of sulphur arises because of different crystal structures. Thus the two major crystalline allotropic modifications of sulphur are *rhombic sulphur* and *monoclinic sulphur*. Both these forms of solid sulphur have S_8 molecular units but these molecular units differ in the crystal morphology. On raising the temperature the S_8 molecular units start to break up into smaller units and under certain special conditions another allotropic form known as *plastic sulphur* is formed.

In general the allotropic modifications of an element exhibit significant differences in their physical properties. Sometimes they even differ somewhat in their chemical properties. As we shall see in passing that these differences in properties of the allotropes are due to a difference in the nature of the chemical bonding. We discuss below the allotropic modifications of four chosen elements—oxygen, sulphur, carbon and phosphorus—and the nature of chemical bonding involved.

10.1.1. Allotropes of Oxygen : Oxygen exists in two allotropic forms : diatomic oxygen and triatomic ozone.

Oxygen : We usually write molecular oxygen with a double bond between two oxygen atoms. As we know (Chapter 1) oxygen atom has a $1s^2\ 2s^2\,2p^4$ electron distribution. Following Pauling we can depict the double bonding in the following way :

$$\begin{array}{lccccc} \textit{oxygen No. 1} & \underset{1s}{\underline{\uparrow\downarrow}} & \underset{2s}{\underline{\uparrow\downarrow}} & \underset{2p_x}{\underline{\uparrow}} & \underset{2p_y}{\underline{\uparrow}} & \underset{2p_z}{\underline{\uparrow\downarrow}} \\ \textit{oxygen No. 2} & \underset{1s}{\underline{\uparrow\downarrow}} & \underset{2s}{\underline{\uparrow\downarrow}} & \underset{2p_x}{\underline{\downarrow}} & \underset{2p_y}{\underline{\downarrow}} & \underset{2p_z}{\underline{\uparrow\downarrow}} \end{array}$$

If we assume that the x axis is the bonding axis then the two electrons of the two p_x orbitals of the two oxygen atoms will overlap to form a strong sigma bond. Sideways overlap of the electrons in the two p_y orbitals will give a pi-bond thus completing the double bond between the two oxygen atoms. Recall that valence bond theory requires that in order that two atoms can interact to form a covalent bond each must possess an unpaired electron and that during overlap of the orbitals the electron spins must be opposed in order to uphold *Pauli exclusion principle.* A consequence of the above type double bonding is that the diatomic oxygen molecule has all paired spins and hence has to be diamagnetic i.e. it will be repelled by a magnetic field. In reality, however, it is found that molecular oxygen is paramagnetic i.e. it is attracted by a magnetic field. Quantitaive evaluation of the magnetic properties shows that for each molecule there are two unpaired electrons. An explanation of this paramagnetic behaviour is found in a molecular orbital description of the diatomic molecule. In Chapter 5 we have given a simple qualitative picture of the molecular orbital theory. x number of atomic orbitals combine to generate x number of molecular orbitals which belong not to any particular atom but to the molecule itself. Half of these M.O.'s are *bonding* i.e. of energy lower than the energy of the original A.O.'s and the other half are *antibonding* i.e. of energy higher than the energy of the A.O.'s. The available electrons are filled in the M.O.'s according to the building-up principle (Chapter 1). Lower energy M.O.'s are filled up first according to Hund's rule and Pauli exclusion principle and thereafter comes the question of filling of the higher energy antibonding M.O.'s. In molecular orbital theory the inner orbitals—in this case the $1s$ orbitals—do not take part. So leaving aside the $1s$ atomic orbitals we take up the M.O. formation of the outer orbitals. The two $2s$ orbitals combine to give two M.O.'s—one bonding σ_{2s} and the other antibonding σ^*_{2s}. Then the two p_x orbitals combine to give two M.O.'s—one is σ_{2px} and the other antibonding σ_{2px}. We have assumed that x axis is the bonding axis. Thereafter comes the interaction of the two degenerate p_y and p_z A.O.'s. This interaction produces two degenerate (i.e. equienergetic) bonding π_{2p} M.O.,s and two antibonding (and degenerate) π^*_{2p} M.O.'s. The order of ,energy and filling of the M.O.'s according to rules give the following picture for O_2.

$$\underset{\sigma_{2s}}{\underline{\uparrow\downarrow}} < \underset{\sigma^*_{2s}}{\underline{\uparrow\downarrow}} < \underset{\sigma_{2px}}{\underline{\uparrow\downarrow}} < \underset{\pi_{2py}}{\underline{\uparrow\downarrow}} \quad \underset{\pi_{2pz}}{\underline{\uparrow\downarrow}} < \underset{\pi^*_{2py}}{\underline{\uparrow}} \quad \underset{\pi^*_{2pz}}{\underline{\uparrow}} < \underset{\sigma^*_{2px}}{\underline{\quad}}$$

It is now quite heartening to see that we are left with two unpaired electrons—one each in the two degenerate antibonding π^*_{2p} M.O.'s. This is good enough an explanation of the paramagnetism of O_2 molecule.

Ozone : In the upper atmosphere, about twelve miles above the surface of the earth, oxygen molecules are excited by ultraviolet rays and are converted to ozone. This is one way living beings on the surface of the earth are saved from too much exposure to ultraviolet rays. In the laboratory oxygen is converted to ozone by silent electric discharge :

$$3O_2(g) \rightarrow 2O_3(g) \; ; \quad \Delta H = +69.0 \text{ KCal (endothermic)*}$$

Table 10.1 records some important physical properties of oxygen and ozone

Table 10.1. Physical Properties of Oxygen and Ozone

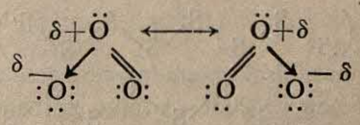
Allotrope	M.P.(°C)	B.P.(°C)	Density (gram/litre)	Solubility in water (mole/lit)
Oxygen	−218	−183	1.429	0.00218
Ozone	−251	−112	2.145	0.00022

As we take up the descriptive chemistry we will observe that ozone is much too active compared to oxygen. It is by far more reactive oxidant than oxygen. The explanation lies in the fact that its heat content is far greater than that of oxygen—note the synthesis is endothermic ! Ozone is a very useful and oft-used oxidant in many organic syntheses.

The three oxygen atoms of ozone are at the apices of an equilateral triangle. The real structure is a resonance hybrid of the structures shown below. Each oxygen is sp^2 hybridised. One electro-pair of an oxygen forms the coordinate link, a second electron-pair remains as a lone pair on the oxygen. The unpaired electron in the third sp^2 hybrid orbital overlaps with a similar sp^2 hybrid orbital of another oxygen. Finally the unpaired electron in the third remaining p orbital of the interacting oxygen atom overlaps with a similar unpaired electron of the other oxygen—thus accounting for the double bond. This bonding pattern resonates among all the three oxygen atoms to produce the final resonance hybrid of O_3. The bond angle and the bond distances are 118° (typical of sp^2 hybridisation) and 1.28A respectively. Note that

$$<O-O-O \simeq 118^\circ \; ; \quad O-O \simeq 1.28A$$

oxygen : $\underset{2(sp^2)}{\uparrow\downarrow} \quad \underset{2(sp^2)}{\uparrow\downarrow} \quad \underset{(2sp^2)}{\uparrow} \quad \underset{2p}{\uparrow}$;



the oxygen-oxygen distance in ozone is intermediate between O−O distance (1.48A) and O = O(1.21A).

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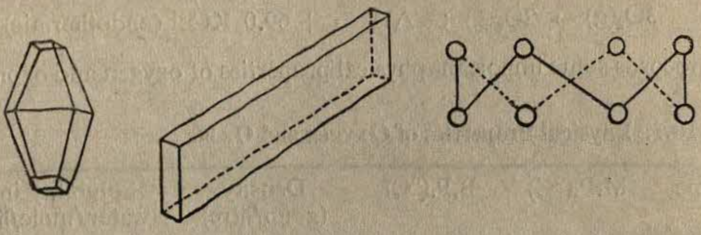
*$\Delta H = H_{\text{products}} - H_{\text{reactants}}$; Hence positive ΔH means H_{product} is larger than $H_{\text{reactants}}$ i.e. an endothermic reaction. On the other hand negative ΔH means an exothermic reaction.

10.1.2. Allotropes of Sulphur : The two major allotropic forms of sulphur are (*a*) *rhombic sulphur* and (*b*) *monoclinic sulphur* (Fig 10.1). Ordinary natural sulphur dissolves readily in CS_2. This solution on slow concentration gives crystals of pure rhombic sulphur. On the contrary when natural sulphur is heated to melting and then allowed to crystallise needles of monoclinic sulphur are obtained. These two allotropes of sulphur remain in equilibrium at around 96°C. The monoclinic form is stable above 96°C while the rhombic form is stable below 96°C. Pure monoclinic sulphur crystals may be obtained by rapid cooling of molten sulphur around its freezing point. In both these forms the element is believed to exist in the *octa-atomic*, S_8, *molecular units*. Above 160°C the viscosity of liquid sulphur changes and its colour deepens from yellow to reddish-brown. It becomes difficult to pour out the viscous liquid. Sudden cooling of the liquid sulphur from above 160°C to room temperature gives yet another allotropic modification, called *plastic sulphur*. The increase in the viscosity is attributed to the breakdown of the S_8 units to give larger-membered chains i.e. *polymers*. In plastic sulphur chains of varying members are present and furthermore these chains are entangled among them. The result is obstruction to free flow—this explains the increase in the viscosity of plastic sulphur (Fig. 10.2.). As the temperature is gradually raised from about 160°C to about 250°C and then towards the boiling point 445°C the polymeric rings are gradually destroyed to smaller units like S_6, S_4 and S_2. The result is obvious : viscosity falls and mobility increases.



rhombic monoclinic S_8 unit

Fig. 10.1. Two major allotropes of sulphur

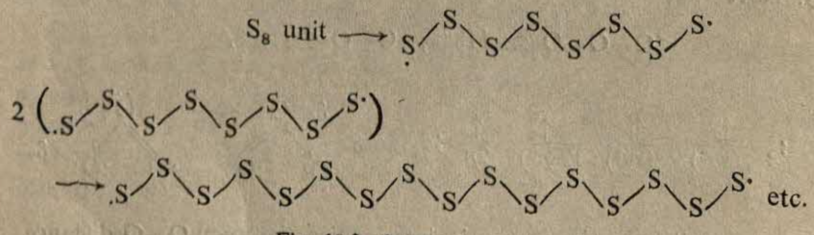
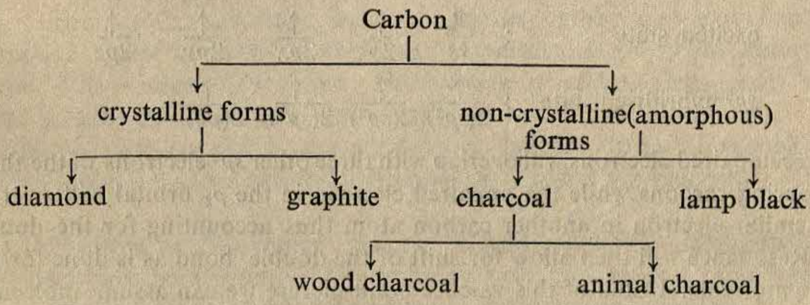


Fig. 10.2. Polymerisation in sulphur

The plastic sulphur that we have mentioned above is not quite stable and changes in course of a few days into the stablest form rhombic sulphur. The sulphur that we usually purchase from the market is a mixture of rhombic sulphur and a non-crystalline amorphous variety.

Structural studies have revealed that the sulphur vapour near its boiling point consists largely of S_2 units. If this sulphur vapour is suddenly cooled to about −196°C it shows paramagnetism—reminiscent of diatomic molecular oxygen. Thus O_2 and S_2 show a parallel magnetic behaviour.

10.1.3. Allotropes of Carbon : By far the largest number of allotropic modifications are encountered in the element carbon. Some of these forms are crystalline in nature while some others are non-crystalline i.e. amorphous. The following classification of the different forms presents a ready appreciation of the area.



Diamond : It may be regarded as a *three-dimensional polymer*. Each carbon atom is bonded to four other carbon atoms placed at the corners of a regular tetrahedron and each of these four carbons is again attached to four more carbon atoms. This pattern is repeated through the crystal lattice thus affording a giant molecule. Since each carbon atom is tetrahedrally disposed it follows that all the carbon atoms are sp^3 hybridised.

$$\text{ground state :} \quad \underset{1s}{\underline{\uparrow\downarrow}} \quad \underset{2s}{\underline{\uparrow\downarrow}} \quad \underset{2p_x}{\underline{\ \uparrow\ }} \quad \underset{2p_y}{\underline{\ \uparrow\ }} \quad \underset{2p_z}{\underline{\quad}}$$

$$\text{excited state :} \quad \underset{1s}{\underline{\uparrow\downarrow}} \quad \underset{2s}{\underline{\ \uparrow\ }} \quad \underset{2p_x}{\underline{\ \uparrow\ }} \quad \underset{2p_y}{\underline{\ \uparrow\ }} \quad \underset{2p_z}{\underline{\ \uparrow\ }}$$

Ground state electronic configuration of carbon is $1s^2\,2s^2\,2p^2$. This is taken to the excited state $1s^2 2s^1, 2p^1, 2p^1 2p^1$, and then the outer orbital electrons are hybridised to the sp^3 state. Overlap of these sp^3 hybrid orbitals each carrying one unpaired electron produces the three-dimensional lattice of diamond (Fig. 10.3)

$$sp^3 \text{ hybridisation :} \quad \underset{2(sp^3)}{\underline{\quad\uparrow\quad}} \quad \underset{2(sp^3)}{\underline{\quad\uparrow\quad}} \quad \underset{2(sp^3)}{\underline{\quad\uparrow\quad}} \quad \underset{2(sp^3)}{\underline{\quad\uparrow\quad}}$$

Extension of the strong covalent bonds throughout the crystal makes it difficult to rupture these bonds. This explains the high melting point (~3600°C) and its great hardness. The carbon-carbon single bond length is 1.54A. Its density is exceedingly high because of the formation of the three-dimensional giant molecule (3.51 gram/ml). It finds ready use in glass cutting.

Graphite : This is another allotrope of carbon which, too, possesses giant molecules. Graphite is, so to say, a *two dimensional sheet polymer*. In between the sheets, which are quite well separated by about 3.4A, there exists only a weak van der Waals force of attraction. The sheets in the graphite structure (Fig. 10.3) may be viewed as fused systems of planar hexagonal benzene rings, each carbon atom being joined to three other carbons in a plane. Each sheet will look like a hexagonal wire netting. Since each carbon is planar and is linked to three others it may be guessed that each carbon is sp^2 hybridised. This same hybridisation also pertains in the benzene ring. The following electron arrangements for the bonding can be written.

ground state	:	$\frac{\uparrow\downarrow}{1s}$	$\frac{\uparrow\downarrow}{2s}$	$\frac{\uparrow}{2px}$	$\frac{\uparrow}{2py}$	$\frac{\quad}{2pz}$
excited state	:	$\frac{\uparrow\downarrow}{1s}$	$\frac{\uparrow}{2s}$	$\frac{\uparrow}{2px}$	$\frac{\uparrow}{2py}$	$\frac{\uparrow}{2pz}$
sp^2 hybridised state	:	$\frac{\uparrow}{2(sp^2)}$	$\frac{\uparrow}{2(sp^2)}$	$\frac{\uparrow}{2(sp^2)}$	$\frac{\uparrow}{2(pz)}$	

The three unpaired electrons will overlap with three other sp^2 electrons of the three neighbouring carbons while the unpaired electron in the p_z orbital will overlap with a smilar electron in another carbon atom thus accounting for the double bond. Resonance will then allow for shift of the double bond as is done for the benzene molecule. Insted of this valence bond picture we can assume molecular orbital formation for the p_z electrons. Each of the six carbon atoms in the hexagonal C_6 unit can combine to generate six molecular orbitals. Of these three will be of the lower energy bonding type and these three will be occupied by the six electrons i.e. by the three electron pairs. On being excited the π electrons can move into the slightly higher energy antibonding molecular orbitals. Such a structure of graphite is capable of explaining several of its properties. Since the π electrons have the liberty of moving into the vacant antibonding M.O.'s it can conduct electric current. The large inter-sheet spacing readily accounts for the low density of graphite (2.22 gram/ml.). The carbon-carbon distance in graphite is 1.415A whereas C$-$C and C $=$ C distances are 1.55A and 1.34A respectively. The corresponding distance in benzene is 1.39A. The sheet structure allows sliding of one layer over the next one. This explains its lubricating properties. The so-called lead pencils are indeed made of graphite. The sheets slide over and allow

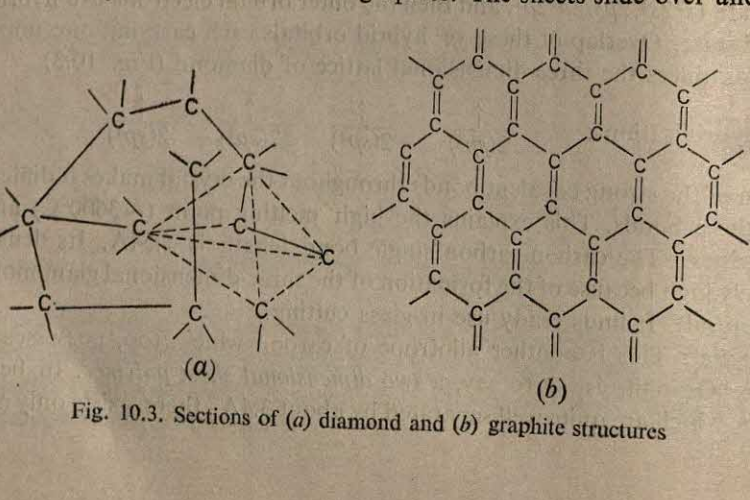


Fig. 10.3. Sections of (a) diamond and (b) graphite structures

marks to be left on the surface of the paper. A comparison of the densities of the two allotropes (graphite, 2.22 ; diamond, 3.51 gram/ml) indicates that proper application of pressure may lead to the transformation of graphite to diamond.

Amorphous carbon : These are the non-crystalline varieties of carbon. The two major forms are (*a*) charcoal and (*b*) lampblack. Destructive distillation of wood i.e. heating of wood in closed iron vessels in the absence of air gives out a large number of very useful byproducts which can be cooled and collected. The black meterial that remains behind after distillation is called *charcoal*, specifically called *wood charcoal*. Similar treatment of animal matter gives *animal charcoal*. Organic materials like petroleum, benzene on heating in the presence of insufficient amount of air gives out a smoke which can be collected as a very fine amorphous material. This is called *lamp black*. This variety of carbon finds ready use in making printing ink, shoe polishing material etc.

Charcoal and lampblack are regarded as inferior forms of graphite. No definite structural pattern like that obtaining in charcoal has emerged.

10.1.4. Allotropes of Phosphorus : Many differently coloured modifications of the element have been described from time to time. However the two most important allotropes are (*a*) white phosphorus and (*b*) red phosphorus.

White phosphorus : This is the most reactive form of the element. It is volatile (M.P. 44°C and B.P. 280°C), inflammable and poisonous. It is soluble in non-polar organic solvents like CCl_4, CS_2. Its structure has been determined. It consists of discrete tetratomic P_4 molecules. Molecular weight determination also supports the P_4 unit. The four phosphorus atoms are situated at the four apices of a regular tetrahedron. The question that puzzles us is : how can we explain such a molecular arrangement? The bond angles $<P-P-P$ are all the same ($\sim 60°$). No hybridisation can account for such a bond angle nor any overlap of pure atomic orbitals. There is no escape from the conclusion that P_4 tetrameric unit is highly strained and deformed. This strained structure, however, helps us to explain why the white phosphorus allotropic form is so very reactive compared to the red variety. Because of its reactivity in air it is stored under water.

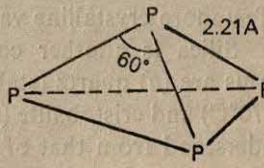


Fig. 10.4 P_4 molecule

Red phosphorus : At 250°C the white phosphorus is converted to the red allotropic form. It is insoluble in non-polar solvents. Its structure is not known with certainty but is believed to be a polymeric form in which each phosphorus is connected to three other atoms. Nothing much is known to carry on the discussion further. Because of the polymeric nature it is not as active as the white form.

10.2. POLYMORPHISM

There are several chemical compounds which can exist in more than one crystalline form. This phenomenon is called polymorphism. When one and the same chemical compound can exist in two crystalline forms it is called *dimorphous* and the phenomenon known as *dimorphism.* When the same compound exists in more than two forms it is called *polymorphous.*

Examples of compounds showing polymorphism and dimorphism are zinc sulphide, ferric oxide, silica etc.

Polymorphism and dimorphism may arise from two factors : (1) The immediate environment of the interacting atoms may remain the same but the relation with the next nearest neighbours may vary. (2) The number of the inter acting atoms may vary to some slight extent inside the unit cell—thereby giving rise to different crystal structures.

1. The best example of the first class is provided by the two crystalline modifications of zinc sulphide. This substance exists in two forms : *zinc blende* and *wurtzite*. In both these crystalline forms the immediate environment is the same—each zinc atom is surrounded tetrahedrally by four sulphur atoms and vice versa. It is in the relation with the next-nearest neighbours that the two forms differ. In zinc blende successive sheets have identical arrangement of zince and sulphur atoms but in wurtzite this arrangement differs. Compared to zinc blende the successive sheets in wurtzite are rotated through 180° about the principal axis.

Carborundum (silicon carbide, SiC) also shows polymorphism. The immediate environment consists of each carbon and silicon atom being tetrahedrally coordinated by atoms of the other kind. Two major polymorphous forms are related to the two forms of zinc sulphide i.e. zinc blende and wurtzite. There are a few more crystalline varieties of carborundum.

Silica is another compound which shows polymorphism. The important forms are (*a*) quartz (stable below 870°C (*b*) tridymite (stable in the range 870-1470°C) and cristobalite (stable above 1470°C). The basic structure can be easily understood from that of diamond. In diamond all the carbon atoms are tetrahedrally linked. We get the internal immediate environment of SiO_2 if we introduce one oxygen atom in between every two carbon atoms in the diamond lattice. Every silicon atom is then surrounded by four oxygen atoms situated at the four corners of a tetrahedron. Each oxygen atom is linked to two silicon atoms opposite to each other. Cristoblite is comparable to zinc blende while tridymite is related to wurtzite structure.

2. Some slight variation in the number of near neighbours in the immediate environment may lead to different crystal structures. An example is found in the α-Fe_2O_3(haematite) and γ-Fe_2O_3. In haematite each iron is surrounded by six oxygen and each oxygen by four iron. The ratio of iron : oxygen is 4 : 6 i.e. 2 : 3. The unit cell of γ-Fe_2O_3 consists of 32 oxygen and an average of $21\frac{1}{3}$ iron. For a perfect spinel type structure $Fe^{3+}[Fe^{2+}\ Fe^{3+}]O_4$ there should have been 24 oxygens.

10.3. ISOMORPHISM

Some compounds are known to crystallise with the same structure. Such compounds are called isomorphous to each other and the phenomenon is known as isomorphism.

Several criteria are to be fulfilled in order that different chemical compounds can be isomorphous to each other :

1. Chemical formulas of the compounds have to be comparable i.e. parallel in nature.

2. There should exist similar chemical bonding in between the interacting atoms of the compounds.

3. Different parts of the compounds, namely the cation, the anion, hydrate water etc. have to be comparable in nature.

4. The total number of atoms making up the compounds should be the same.

5. The sizes of the ions of the different compounds should be close and the charges must be the same.

When the above conditions are fulfilled we may expect different compounds to crystallise in the same structural forms. For example $CoSO_4.7H_2$ and $NiSO_4.7H_2O$ are isomorphous to each other. Note that both the compounds contain bipositive cations of almost the same ionic radii, both have the binegative sulphate anions and both possess the same number of hydrate water. Both have a total of 27 atoms. So all the conditions of isomorphism are fulfilled and hence both the compounds have the same crystal structures. Below we give a classification of different isomorphous compounds :

I. *Alums* : These are double sulphates of trivalent and monovalent cations with twelve molecules of water. Their general formulas are $M^IM^{III}(SO_4)_2.12H_2O$ (also written as $M^I{}_2SO_4.M^{III}{}_2(SO_4)_3.24H_2O$) where M^I stands for unipositive cations NH_4^+, Na^+, K^+, Rb^+, Cs^+ and M^{III} represents a tripositive cation like Al^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Co^{3+} etc. However not all the above combinations may give rise to the formation of alums. Also it may be noted that lithium ion although monopositive does not form any alum presumably because of its comparatively small size.

II. *Schonites* : These are the double sulphates of monopositive and bipositive cations, which crystallise with six molecules of water. Their general formulas are $M^I{}_2M^{II}(SO_4)_26H_2O$. The monopositive cation may be one of NH_4^+, Na^+, K^+ etc. while the bipositive cation may be one of the ions Fe^{2+}, V^{2+}, etc.

III. *Vitriols* : These are the sulphates of bipositive cations which crystallise with seven molecules of water. Common examples are $FeSO_4.7H_2O$, $NiSO_4.7H_2O$, $CoSO_4.7H_2O$ etc. Strictly speaking $CuSO_4.5H_2O$, although commonly called a *blue vitriol*, is not a vitriol as it does not crystallise with $7H_2O$. It is in fact not isomorphous with any of the true vitriols.

IV. *Sulphates, selenates and chromates* : These anions are parallel in their composition : SO_4^{2-}, SeO_4^{2-}, CrO_4^{2-}. Salts of these anions with the same cation are isomorphous. Thus K_2SO_4 and K_2CrO_4 are isomorphous. $BaSO_4$ and $RaSO_4$ are isomorphous. K_2CrO_4 and K_2FeO_4 are also known to be isomorphous to each other.

Evidence in favour of isomorphous behaviour : (1) Complete X-ray crystallographic structural studies of a compound provides authentic data on the different bond lengths and bond angles. If two compounds are isomorphous then these will provide very close and comparable X-ray data on the bond lengths and bond angles. However such examination is time consuming. (2) One chemical way of testing isomorphous character is via formation of *mixed crystals*. Since the compounds are isomorphous they are expected to crystallise in the same structural forms. Given favourable solubility relation it may be possible to prepare a solution of the two compounds in a known ratio. Such a solution on being allowed to crystallise will furnish crystals of both the compounds in the same ratio they were originally present in the solution. Formation of mixed crystals is thus a good chemical test of isomorphism. Interestingly if we suspend a big good crystal of potassum chromium alum into a saturated solution of potassium aluminium alum there will be growth of crystals of potassium aluminum sulphate round the suspended crystal of potassium chromium sulphate.

10.4. ALLOTROPY AND ISOMERISM

Allotropy refers to different modifications of one and the same element in the same physical state. Isomerism is the phenomenon by virtue of which compounds having the same empirical composition possess different properties and molecular structures. Thus two or more different compounds having the same formula are called isomers. Thus we see allotropy refers to different forms of an element while isomerism refers to different forms of compounds with the same composition.

Diatomic oxygen, O_2, and triatomic oxygen, O_3, are two different forms of the same element oxygen. Hence they are allotropes. But ethyl alcohol, CH_3-CH_2-OH, and dimethyl ether, CH_3-O-CH_3, are two different compounds but have the same empirical composition C_2H_6O. These two are therefore isomeric to each other. Ammonium cyanate NH_4OCN and urea $CO(NH_2)_2$ have entirely different properties although they have the same empirical composition. Similarly *cis* and *trans* $[Pt(NH_3)_2Cl_2]$ have the same empirical composition but entirely different structural disposition. In the *cis* variety the two chloride groups (and hence the two NH_3 groups as well) are near neighbours about square planar platinum (II) whereas in the *trans* the groups are diagonally disposed along the square plane.

10.5. ALLOTROPES AND ISOTOPES

Both allotropes and isotopes refer to elementary states. Isotopes are different species of the same element such that they differ only in atomic weights. They have the same atomic number and hence the same number of protons but different number of neutrons in the nucleus. Allotropes are also different modifications of the same element, which arise out of varying number of atoms in the molecules or out of entirely different type of bonding in the molecules. Varying number of neutrons in the nuclei cannot influence allotropy i.e. isotopes cannot influence formation of the allotropic modifications. To take a simple example diatomic oxygen, O_2, and triatomic ozone, O_3 are made of oxygen-16 and oxygen-18 isotopes. In diamond and graphite there will be hardly any change if we substitute the common carbon-12 by the rather rare carbon-14. Allotropy of sulphur may be realised by both sulphur-32 and sulphur-35.

EXERCISES

1. What is allotropy? Does it apply to both elements and compounds?

2. Explain the two major allotropic modifications of carbon from the standpoint of chemical bonding.

3. Give a resume of the allotropy of carbon, sulphur and oxygen.

4. Both diamond and graphite form giant molecules but that the natures of their bonding are quite different. Explain.

5. Is there any connection between allotropy and isomerism? In some old texts it is written that isomerism is a form of allotropy. Do you agree?

6. Isotopes and allotropes are manifestations of the elementary states. Where do they really vary?

7. What is isomerism? Name some compounds which exhibit isomerism.

8. What is isomorphism? What are the basic requirements for two compounds to be isomorphous with each other. Name some compounds which are isomorphous.

9. $NiSO_4.7H_2O$ and $ZnSO_4.7H_2O$ are vitriols and are isomorphous. But the so called blue vitriol $CuSO_4.5H_2O$ has a different composition. Do you think the copper salt will be isomorphous with the nickel and zinc salts?

10. Mixed crystal formation between two different compounds is a test of isomorphism. Elucidate.

CHAPTER 11

ATOMIC WEIGHTS AND MOLECULAR WEIGHTS

11.1. WE GO BACK TO THE OLDEN DAYS

John Dalton had proposed in his atomic theory that all elements were composed of very tiny particles which he named *atoms*. He had also suggested that atoms of different elements had different atomic weights (in fact masses). He was quite aware of the fact that much of the future progress in chemistry and in science in general must depend on our ability to determine with precision the atomic weights. It was impossible, however, to pick out the atoms separately and weigh them directly to evaluate the atomic weight. Thus he knew that one would have to take recourse to indirect method for such determination.

Dalton also knew that different elements reacted in definite proportion to form chemical compounds. Thus 23.00 gram of sodium always reacted with 35.5 gram of chlorine to form the compound sodium chloride. Whatever the amount of sodium chloride formed and whatever their sources were the interacting ratio was always the same i.e. 23.00 : 35.50. This experimental fact provided him with a clue that the atoms of these elements must also be reacting in a definite ratio. In other words chemical elements must be reacting in definite ratio of their atomic weights. He was thus convinced that studies on the formation of different chemical compounds from chosen elements would someday lead to the evaluation of the atomic weights.

Further quantitative progress in chemical science rested on the precise determination of the atomic weights of the various elements. Although Dalton was a pioneer in this area very many chemists of the nineteenth and the early twentieth centuries have vigorously contributed to this area. Notable among these people are : Berzelius (1779-1848 ; Stockholm), Dumas (1800-1884 ;), Madame Curie (1867-1934 ; Sorbonne) ; Cannizaro (1826-1910 ; Genoa, Palermo and Rome) and Richards (1868-1928 ; Harvard).

11.2. SOME PRELIMINARIES ABOUT ATOMIC WEIGHTS

Atomic weights are relative to certain element taken as a standard. As we shall run through this Chapter we shall see that from time to time this standard element was changed from hydrogen to oxygen and finally to carbon. Hydrogen was initially preferred because it is the lightest element known and could naturally stake its claim as the standard. Thereafter it was observed that there were quite a large number of elements which did not react with hydrogen to give compounds of definite composition. The next choice was oxygen and rightly so because oxygen was found to react with a very large number of elements to give oxides of known composition. However an interesting problem cropped up with oxygen. With the discovery of mass spectrograph by Aston it was possible to analyse the mass (or rather loosely the atomic weight) of an element. It was found that the chemists' standard oxygen-16 against which chemists have determined so many atomic weights so vary laboriously is no longer an un-objectionable element. It has a heavy isotope oxygen-18 to some slight extent. Physicists held out the view that whatever standard is used in fixing the atomic weight it must be done against a standard of fixed and invariable mass. Physicists' stand was that chemists' standard oxygen-16 is really not oxygen-16 but a little heavier than mass 16. This meant that the chemists' atomic weights had to be recalculated on the basis of this new finding. The mass of oxygen-16 was 16 but that of natural oxygen, against which chemists had done all their calculations, was 16.00447, taking into account the natural abundances of the oxygen-17, oxygen-18 and of course oxygen-16 isotopes. The sum-total result was that chemical atomic weights determined against natural oxygen taken as oxygen-16 was lower by a factor 16.00000/16.00447. This agitated the entire chemical world because the revisions of the atomic weight data would mean revision of all other important thermodynamic and other relevant data. Then the chemists were out to find some other standard where isotopic effect on mass i.e. on atomic weight will be truly negligible. They were heartened to discover that carbon held for them the answer. This element has three isotopes : carbon-12, carbon-13 and carbon-14 but the percentage of the heavier two isotopes is such that they were not of much consequence to change the chemically determined carbon mass from 12.011617 to any higher value for all practical purposes. So till date the position is that we express all our atomic weights in terms of the carbon-12 isotope.

Atomic weight : Atomic weight of an element really means a number which indicates how heavy an atom of a particular element is compared to an atom of a standard element. Thus atomic weight is just a dimensionless ratio i.e. number. Since carbon-12 is the accepted standard we can define atomic weight in the following terms :

Atomic weight of an element is a number that indicates how heavy an atom of a particular element is compared to 1/12*th of a carbon*-12 *atom.*

Atomic mass unit (*amu*) : Although, as mentioned above, atomic weights are just numbers chemists often express these numbers in *atomic mass units* (*amu*) ; *Atomic mass unit is exactly the* 1/12*th of the mass of a carbon*-12 *atom.* Thus the mass of an atom in *amu* is numerically equal to the atomic weight expressed in the carbon-12 scale. What is the value of this *amu* in grams ?

Value of amu in grams : One gram mole of carbon-12 weights exactly 12 grams. Again one gram mole has 6.023×10^{23} atoms of carbon-12. Thus an atom of carbon-12 weighs $12/(6.023 \times 10^{23})$ gram. Again an atom of carbon-12 weighs 12 *amu*. Therefore :

$$1\ amu = \frac{12}{(6.023 \times 10^{23}) \times 12} = 1.6603 \times 10^{-24} \text{ gram}$$

Given below are the atomic weights of a few common elements in *amu* :

Hydrogen = 1.007967 : Oxygen = 15.99943
Nitrogen = 14.007 : Carbon = 12.01115
Boron = 10.81 : Sodium = 22.9898

When we say that nitrogen has an atomic weight of 14.007 in the carbon-12 scale we really mean that an atom of nitrogen is 14.007 times heavier compared to 1/12th of a carbon-12 atom.

Gram atomic weight : Gram atomic weight of an element is that weight in gram that carries the same number (i.e. 6.023×10^{23}) of atoms as are present in 12 grams of carbon-12. Effectively gram atomic weight of an element is the atomic weight (in *amu*) expressed in gram. Thus the gram atomic wight of nitrogen is 14.007 gram. One gram atomic weight or more simply one gram atom contains 6.023×10^{23} atoms.

11.3. GAY LUSSAC PUTS DALTON IN A DILEMMA

Dalton was one of the first scientific personnels who went for the evaluation of the atomic weights of different elements. His choice of a standard fell on hydrogen—this being the lightest in the entire family of elements. He determined the composition of several compounds of which water merits discussion. He determined that 8 gram of oxygen reacted with 1 gram of hydrogen. Assuming that hydrogen had an atomic weight 1 he concluded that the atomic weight of oxygen was 8. This meant hydrogen and oxygen reacted in 1 : 1 ratio. In other words formula of water was HO. A little thought will tell us that unless we know the interacting atomic ratio we cannot fix the atomic weights. Thus if water does have the formula HO Dalton's determination of the atomic weight of oxygen as 8 appears justified. If the formula were H_2O then the atomic weight of oxygen stood to be 16. It thus appears that more than one synthetic route for one particular compound and composition studies of more than one compound having a common element are essential to arrive at reliable atomic weight values.

In the course of evaluation of the weight compositions of compounds the following two laws were established :

1. *The law of definite composition* : *Elements in a compound are always present in definite proportions by weight.* Thus no matter what is the source of sodium chloride or what is the synthetic route adopted every 23.00 gram sodium react with 35.5 gram of chlorine.

2. *The law of multiple proportions* : *When two elements react to give more than one compound then with the weight of one being fixed the weight of the other varies in small whole numbers.* Thus in carbon monoxide and carbon dioxide for every 12 gram of carbon the weights of oxygen are 16 and 32 gram respectively. Thus the ratio of carbon : oxygen in carbon monoxide and dioxide are 1 : 1 and 1 : 2 respectively.

We have observed that it was not possible for Dalton to decide (according to our present day judgement) unambiguously whether the formula of water was HO or H_2O. At the turn of the nineteenth century Gay Lussac had been doing commendable research on the combining ratios of gases. In 1808 he proposed : *The volumes of reactant gases and product gases are in small whole numbers. In other words during chemical combination gases maintain a simple relationship in their volumes.* This generalisation is known as *Law of Combining Volumes.* Thus ;

1 volume of hydrogen + 1 volume of chlorine → 2 volumes of hydrogen chloride
2 volumes of hydrogen + 1 volume of oxygen → 2 volumes of water vapour or steam

Dalton tried to correlate Gay Lussac's observations in the light of his atomic theory. He argued like this : a particular volume of a gaseous element must contain a number of particles i.e. atoms. If there is really a simple relationship in the combining volumes of the gases there must be a similar simple relationship between the number of atoms of the combining gases. For elementary gases Dalton assumed that the particles that participated in chemical reactions were single atoms. He assumed the product gases to have atoms of different nature combined chemically. All these led him to a blind lane where he himself was in a dilemma :

2 volumes of hydrogen + 1 volume of oxygen → 2 volumes of steam
2 atoms of hydrogen + 1 atom of oxygen → 2 atoms of steam
1 atom of hydrogen + $\frac{1}{2}$ atom of oxygen → 1 atom of steam

Thus we see that slicing of an oxygen atom is necessary if we are to accommodate Gay Lussac's Law of Combining Volume in the light of Dalton's theory. But one of the pillars of Dalton's atomic theory is that atoms are indivisible entities. How then to tide over the apparent dilemma ?

11.4. AMEDEO AVOGADRO COMES TO OUR RESCUE

Three years after Gay Lussac proposed his Law of Combining Volumes there appeared in 1811 in the scientific arena an Italian genius, Amedeo Avogadro by name. He made two very outstanding statements :

1. *Avogadro hypothesis* : *Under a given condition of temperature and pressure, equal volumes of gases contain equal number of particles.*

2. *Gaseous elements exist as diatomic molecules* : After a careful examination of Gay Lussac's results on reactions of gases Avogadro came to the above conclusions. When these ideas were translated into practice Avogadro's hypothesis meant 'equal volumes — equal molecules'. Then Gay Lussac's experiments may be re-written as :

1 volume of hydrogen + 1 volume of chlorine → 2 volumes of hydrogen chloride
1 molecule of hydrogen + 1 molecule of chlorine → 2 molecules of hydrogen chloride
$\frac{1}{2}$ molecule of hydrogen + $\frac{1}{2}$ molecule of chlorine → 1 molecule of hydrogen chloride
1 atom of hydrogen + 1 atom of chlorine → 1 molecule of hydrogen chloride

Similarly we can work out the formation of water from hydrogen and oxygen :

2 volumes of hydrogen + 1 volume of oxygen → 2 volumes of steam
2 molecules of hydrogen + 1 molecule of oxygen → 2 molecules of steam
1 molecule of hydrogen + $\frac{1}{2}$ molecule of oxygen → 1 molecule of steam
2 atoms of hydrogen + 1 atom of oxygen → 1 molecule of steam

The above applications of Avogadro's ideas to the experiments gave us two important conclusions :

1. *Dalton's atom remains indivisible*
2. *Chemical formula of water is H_2O and not HO.*

11.5. WHAT REALLY IS THE BASIS OF AVOGADRO'S HYPOTHESIS ?

Avogadro's hypothesis has a firm foundation in the kinetic molecular theory of gases. Pressure exerted by a gas is due to its kinetic motion. Two factors determine the magnitude of the pressure : (1) force per collision and (2) number of collisions per unit area.

$$\text{Pressure} = \frac{\text{force}}{\text{collision}} \times \frac{\text{number of collisions}}{\text{unit area}} = \frac{\text{force}}{\text{unit area}}$$

The number of molecular collisions per unit area is dependent on the molecular velocities. The greater the velocity the faster the molecules strike the walls of the container vessel. Thus we can write that P, the gas pressure, varies directly as the velocity v :

$$P \propto v$$

But then the force is also dependent on how heavy the gas molecule is i.e. on its mass. In other words the pressure P is dependent on the product of the mass, m, and the velocity v i.e. on mv, the *momentum* of the molecules. Then we can write :

$$P \propto v \; ; \; P \propto mv \; ; \; P \propto mv^2$$

If the product of the mass and the square of the velocity are the same for different gases then the pressure exerted will be the same.

Long before his proposing the Law of Combining Volumes Gay Lussac had inunciated another Law : The pressure exerted by a constant weight of a gas, at constant volume, varies directly with the absolute temperature. Let us assume the following characteristics of a gas :

n = number of gas molecules ; P = total gas pressure
m = weight of a gas molecule ; V = total volume of the gas
v = volume of a gas molecule ; T = absolute temperature

Then we can write the following relations :

(1) $P \propto mv^2$ (for constant n, V, T)
(2) $P \propto T$ (for constant n, V)
Thus $mv^2 \propto T$ (for constant n, V, P)
$\therefore mv^2 = \text{a constant}. T$ (for constant n, V, P)

If different gases are to have the same mv^2 they must be at the same absolute temperature i.e. the relation tells us that at constant absolute temperature and constant pressure equal volumes of different gases must have the same number of molecules i.e. particles. So we see that Amedeo Avogadro had done a monumental piece of work in the development of fundamental ideas of science.

11.6. DETERMINATION OF ATOMIC WEIGHTS

11.6.1. Determination of atomic weights of gaseous elements : A combined application of Gay Lussac's Law of Combining Volumes and Avogadro's pronunciation of the diatomicity of gaseous elements afforded a ready method of evaluation of the atomic weights of these elements.

Atomic weight of oxygen : We have already seen that 8 parts by weight of oxygen combine with 1 part by weight of hydrogen to form water or steam. Again according to Gay Lussac's Law and Avogadro's statement we have :

2 volumes of hydrogen + 1 volume of oxygen → 2 volumes of steam
2 volumes of hydrogen + 1 volume of oxygen → 2 volumes of steam
1 molecule of hydrogen + $\frac{1}{2}$ molecule of oxygen → 1 molecule of steam
2 atoms of hydrogen + 1 atom of oxygen → 1 molecule of steam

Thus the formula of water turns out to be H_2O. Hence we see that 2 parts by weight of hydrogen react with $2 \times 8 = 16$ parts by weight of oxygen. *Thus we conclude that the atomic weight of oxygen is* 16.

Atomic weight of nitrogen : Quantitative studies on the formation of ammonia from hydrogen and nitrogen furnish us the following data :

3 volumes of hydrogen + 1 volume of nitrogen →2 volumes of ammonia
3 molecules of hydrogen + 1 molecule of nitrogen→ 2 molecules of ammonia
3/2 molecules of hydrogen + $\frac{1}{2}$ molecule of nitrogen→ 1 molecule of ammonia
3 atoms of hydrogen + 1 atom of nitrogen→ 1 molecule of ammonia

Thus the molecular formula of ammonia is NH_3. Experimentally it is known that 6 parts by weight of hydrogen react with 28 parts by weight of nitrogen i.e. 3 parts by weight of hydrogen react with 14 parts by weight of nitrogen. Since in the molecular formula of ammonia 3 atoms of hydrogen are present per atom of nitrogen we conclude that the atomic weight of nitrogen is 14.

11.6.2. Atomic weights from vapour density of gaseous compounds : Density is defined as *mass per unit volume*. The unit is *gram per millilitre*. Since volume is dependent on temperature and pressure the standard conditions are 0°C and 76 cm. of mercury. Under these standard conditions one millilitre of hydrogen weighs 0.00009 gram. Thus standard density of hydrogen is 0.00009 gram. Standard densities of other gaseous compounds are also rather small numbers. Hence the standard densities of such compounds are expressed as multiples of standard density of hydrogen. These figures therefore indicate how heavy the compound is compared to hydrogen. These relative figures are also known as *vapour density* :

$$\text{Vapour density } (D) \text{ of a gaseous compound} = \frac{\text{mass of } x \text{ ml of the compound}}{\text{mass of } x \text{ ml of hydrogen}}$$

Applying Avogadro's 'equal volumes — equal molecules" rule we have :

$$\text{Vapour Density } D = \frac{\text{mass of } n \text{ molecules of the compound}}{\text{mass of } n \text{ molecules of hydrogen}}$$

Since hydrogen molecule is diatomic we can write :

$$\text{Vapour Density } D = \frac{\text{mass of } n \text{ molecules of the compound}}{\text{mass of } 2n \text{ atoms of hydrogen}}$$

But then taking hydrogen as the standard, molecular weight of a compound may be defined as a number that indicates how heavy a molecule of the compound is compared to an atom of hydrogen.

$$\text{Vapour Density } D = \tfrac{1}{2} \times \frac{\text{mass of 1 molecule of the compound}}{\text{mass of 1 atom of hydrogen}}$$

$$= \tfrac{1}{2} \times \text{molecular weight of the compound} = \tfrac{1}{2} M$$

Thus $M = 2D$

Once we know experimentally the value of the vapour density we can calculate the molecular weight of the compound. Thereafter we have to have a knowledge of the empirical formula of the compound so that the atomic weight of the desired element can be evaluated.

Atomic weight of carbon from vapour density of methane : Experiments show that the standard density of methane is 0.7168 gram/liter and that for each carbon there are four hydrogen atoms.

Density per millilitre of methane = 0.7168/1000 = 0.0007168 gram/ml

Vapour Density D = Density of methane/Density of hydrogen

= 0.0007168/0.00009 = 8.0

Thus the molecular weight of methane = 2×8.0 = 16.0

Atomic weight of carbon = molecular weight of methane − 4 × atomic weight of hydrogen = 16 − 4 × 1 = 12.

Atomic weight of carbon from vapour density of ethylene : Experimental results give vapour density as 14 and that for every carbon there are two hydrogens. Percentage of carbon is 85.7.

Since the vapour density is 14 the molecular weight of ethylene has to be 2×14 = 28. Since the percentage of carbon is 85.7 the total amount of carbon present in one gram mole of ethylene is (85.7×28)/100 = 24. If we take the formula of ethylene as CH_2 then the atomic weight of carbon may appear to be 28 − 2 = 26. This result is at variance with what we have derived from examination of methane, which gave the atomic weight as 12. Atomic weight of an element cannot vary but due to the Law of Multiple proportions the same element may combine with a second element to give more than one compound. The minimum value from several such determinations has to be accepted as the atomic weight. From the percentage of carbon in ethylene we have an apparent value of 24 as the atomic weight. If we divide this value by 12 derived from methane we find that ethylene has two carbons and therefore four hydrogens. Thus the formula of ethylene is C_2H_4 and not CH_2.

Apparent inconsistencies in Dumas' work and present-day explanations : Although Avogadro's deductions proved very useful for a large many compounds its inconsistency was pointed out by some studies of the French chemist Dumas. He investigated the vapour densities of phosphorus, sulphur, arsenic and mercury. The atomic weights that he derived on the basis of the diatomicity proposed by Amedeo Avogadro appeared inconsistent with other experimental work. We now know neither Dumas nor Avogadro was wrong. Unfortunately for Dumas he chose just those elements which we know today to be forming either monoatomic species (cf : mercury) or polyatomic species (cf : P_4, As_4, S_8, S_6, S_4, S_2). Amedeo Avogadro's deductions have stood the test of time.

11.6.3. Dulong and Petit's Law : While developing his atomic theory Dalton thought if one could get at two amounts of two different elements having the same number of atoms then the ratio of the two weights would give the ratio of their atomic weights. However it was impractical for all purposes and Dalton himself realised this. However this idea was made use of by Dulong and Petit in a somewhat different form. They hit upon the idea that the heat required to raise the temperature of a substance by 1°C should be dictated by the number of the atoms rather than by the character of the atoms. If the number of atoms involved be maintained the same, say the Avogadro number, then the heat required in the case of different elements should turn out to be nearly the same. *Specific heat of an element is defined as the heat required to raise the temperature of* 1 *gram of the element by* 1°C. *Dulong and Petit found that the product of the specific heat and the gram-atomic weight of an element was always close to* 6 *Cal/*°C. Note that this product is the total heat necessary to raise the temperature of one gram-atom of the element by 1°C and is known as the *molar heat capacity*. The constancy of the molar heat capacity indeed showed that this was dictated more by the number of atoms of the element concerned rather than by the properties of the atoms.

Thus the Dulong and Petit Law provided yet another method of determining the atomic weight of an element. If the specific heat is carefully determined and then 6 is divided by the specific heat we will get the atomic weight of the desired element. However the accuracy of the method is not very high—usually an error of around ± 10% is involved. Table 11.1 gives some data obtained by Dulong and Petit.

Table 11.1. Some Data on Dulong and Petit's Law

Element	gram-atomic weight	specific heat	gram-atomic weight × specific heat
Na	23.0 gram	0.295 Cal/g°C	6.79 Cal/°C
Mg	24.3 ,,	0.246 Cal/g°C	5.98 Cal/°C
Ca	40.0 ,,	0.155 Cal/g°C	6.21 Cal/°C
Cu	63.5 ,,	0.0921 Cal/g°C	5.83 Cal/°C
Ag	108.0 ,,	0.0558 Cal/g°C	6.02 Cal/°C

11.6.4. Determination of atomic weights from equivalent weights : We have already remarked that the accuracy of the atomic weights from Dulong and Petit's Law is not very good. However a combination of the experimentally determined equivalent weights and atomic weights from the Dulong and Petit's Law provides a reliable value of the atomic weight. Gram equivalent weight of an element may be defined as that weight which combines or corresponds to 1 gram of hydrogen or 8 grams of oxygen. Electrochemically it may be defined as that weight which is deposited at the cathode or dissolved out from the anode during the passage of one *Faraday* of electricity. Again gram atomic weight divided by the equivalent weight gives the valence of the element concerned. *Valence has to be a whole number — it cannot be a fraction.* Thus we take the gram atomic wieght from Dulong and Petit's Law and divide this by the gram equivalent weight. Thus the valence is obtained. The figure for valence thus obtained is rounded off to the nearest whole number. After we have determined the integer valence then the experimentally determined equivalent weight is multiplied by the integer valence to arrive at a good value of the gram-atomic weight.

$$\text{gram atomic weight} = \text{gram equivalent weight} \times \text{valence } n \; (n = 1, 2, 3 \text{ ..etc.})$$

11.6.5. Determination of Atomic Weights by Chemical Methods : There is no hard and fast rule about how to proceed for the determination of atomic weight by chemical methods. Usually reactions of the types (1) synthesis (2) decomposition and (3) substitution are made use of. In general an idea of the chemical formula of a compound containing the element whose atomic weight is being sought is necessary. We will take up two examples to illustrate the procedures.

I. A known weight of the element whose atomic weight is to be determined is reacted with another element whose atomic weight is known with certainty and with which a compound of definite formula is formed.

Problem 1 : 3.4602 grams of a trivalent element is reacted with an excess of of oxygen to give 4.4031 gram of an oxide. Calculate the atomic weight of the element X.

Since the element is trivalent the formula of the oxide is X_2O_3.

$$2\,X + 3O \rightarrow X_2O_3$$

Let us assume that the atomic weight of the element X is x. Then the weight of the reactants is $2x + 3 \times 16.00 = 2x + 48$. Therefore we can write the following relation :

$$\frac{2x + 48}{2x} = \frac{4.4031}{3.4602}$$

Therefore $2x(4.4031 - 3.4602) = 48 \times 3.4602$

$$2x = \frac{48 \times 3.4602}{0.9429} = 176.1 \; ; \; x = 88$$

II. A certain weight of a chemical compound of the element whose atomic weight is to be determined is reacted with another compound to give a second chemical compound. The weight of the new product is carefully recorded. Then these reactions and the weights can be manipulated to get the atomic weight of the element.

Problem 2 : 4.0231 gram of the oxide of a bivalent element X is reacted with H_2SO_4 and 8.6361 gram of a pure sulphate is obtained. Calculate the atomic weight of the element X.

Since the element involved is a bipositive one we can write the following reaction :

$$XO + H_2SO_4 \rightarrow XSO_4 + H_2O$$

Let x be the atomic weight of the element X. Atomic weights of oxygen and sulphur are too well-known.

Molecular weight of $XO = x + 16.00$

Molecular weight of $XSO_4 = x + 32.06 + (16.00 \times 4) = x + 96.06$

Then the ratio of the two compounds XO and XSO_4 will be as under :

$$\frac{XO}{XSO_4} = \frac{x + 16}{x + 96.06} = \frac{4.0231}{8.6361}$$

$$x(8.6361 - 4.0231) = (96.06 \times 4.0231) - (16 \times 8.6361)$$

$$x = \frac{386.4590 - 138.1776}{4.6130} = 53.82$$

Thus the atomic weight of the element X works out to be 53.82

11.6.6. Determination of Atomic Weights via Isomorphism : We have earlier seen that under certain conditions two chemical compounds can show isomorphous behaviour. If we have two such compounds and if the molecular weight of one is known then it is possible to calculate the atomic weight of another element forming the second of the isomorphous compounds. We know that K_2SO_4 and K_2CrO_4 are isomorphous salts. Below we demonstrate how isomorphism can be utilised to determine the atomic weight.

Problem 1 : Potassium sulphate and potassium chromate are isomorphous. Analysis of potassium chromate gives 26.7% chromium. Calculate the atomic weight of chromium.

Since potassium sulphate and potassium chromate are isomorphous their compositions are also similar i.e. K_2SO_4 and K_2CrO_4. The atomic weights of potassium, sulphur and oxygen are 39, 32 and 16 respectively.

Molecular weight of $K_2CrO_4 = (2 \times 39) + x + (4 \times 16) = 142 + x$

Percentage of chromium $= \dfrac{x \times 100}{x + 142} = 26.7$

$$(100 - 26.7)\, x = 142 \times 26.7 \; ; \; \therefore \; x = 52$$

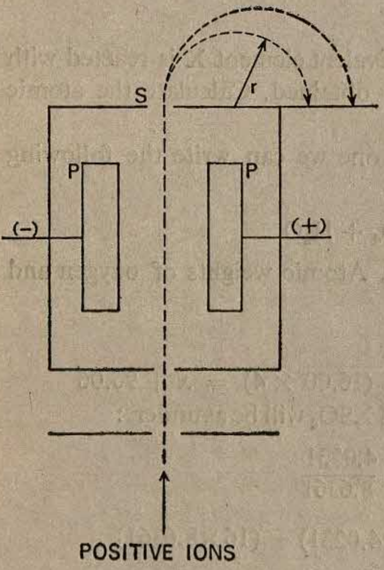


Fig. 11. 1
Bainbridge's mass spectrograph

11.6.7. Physical Method : Mass Spectrograph : We have already seen in Chapter 2 how Aston developed a mass spectrograph instrument for identification of particles with different e/m ratios. Here we describe yet another instrument developed by Bainbridge for a similar purpose. In Aston's instrument positively charged particles were first led through an electric field and then through a magnetic field. The two fields were applied in the same plane but in opposite direction. In Bainbridge apparatus the gaseous element is first introduced into an ionisation chamber where these are bombarded with electrons. This results in the formation of positive ions of the element. These ions are then led through fine slits into a chamber where the ions are subjected to simultaneous electric and magnetic fields working in opposition (cf: Fig. 11.1. Plates PP indicate the electric field ; magnetic field not shown). It is so arranged that only those particles which have the same velocity emerge at the slit S. If the strengths of the magnetic and the electric fields are H and X respectively and e and v the charge and velocity then for the particles coming out at the slit S we have :

$$Hev = Xe \quad ; \quad v = X/H$$

All other particles with different velocities will be retained inside the chamber where the electric and magnetic fields are being applied simultaneously in opposite direction. Now the particles emerging out through the slit S are again subjected to another strong magnetic field (not shown in Fig. 11.1). Here the particles assume a semicircular path : The radius of this path (r) follows the relation :

$$r \propto m/ne \quad ; \quad r \propto m \text{ (when charge } ne \text{ is equal to 1)}$$

Thus particles with a smaller mass will have a trajectory of smaller radius and those with larger mass a trajectory of larger radius. Thus if we standardise the instrument with an isotope of known mass (O−16) and determine the radius of its trajectory with the help of a photographic plate then it is possible to determine the mass of other elements with respect to O−16 as the standard.

11.6.8. Some Problems Related to Atomic Weights :

Problem 1 : 2.00 gram of nickel oxide was reduced by hydrogen and 1.5720 gram of the metal was obtained. What is the equivalent weight of the metal ?

Equivalent weight of an element is that weight which combines with 8.00 gram of oxygen.

Amount of nickel = 1.5720 gram ; amount of oxygen = 2.000 − 1.5720
= 0.428 gram

Equivalent weight of nickel = (1.5720×8)/0.428 = 29.4 gram

Problem 2 : Specific heat of nickel is 0.104 Cal/g°C. Give an approximate idea about the atomic weight of the metal.

According to Dulong and Petit's Law we have :

specific heat × gram atomic weight = 6 Cal/°C

gram atomic weight = (6 Cal/°C)/0.104 Cal/g°C = 58 gram

Problem 3 : In a gaseous hydrocarbon the percentages of carbon and hydrogen are 92.3% and 7.7% respectively. 628 ml of this gas weighs 2.20 gram. Gram atomic weights of carbon and hydrogen are 12.0 and 1.01 respectively. Determine the exact formula of the compound.

Since we are provided with the percentages we first work out the gram atoms present per 100 gram of the sample. The ratio of these two gram atoms will give us the empirical (but not necessarily the true) composition.

Gram atoms of carbon = 92.3/12.0 = 7.69 per 100 gram of the sample
Gram atoms of hydrogen = 7.7/1.01 = 7.60 per 100 gram of the sample
So the atom ratio is carbon : hydrogen = 7.69 : 7.60 = 1.0
The empirical composition is CH.

Standard density of the hydrocarbon = 2.20 gram/628 ml = 0.0035 gram/ml
Standard density of hydrogen = 1.01/22.4 litre = 0.000089 gram/ml
Relative or the vapour density of the hydrocarbon = 0.0035/0.000089 = 39.3
Therefore the molecular weight of the hydrocarbon = 2×vapour density
= 2×39.3 = 78.6

The formula weight of CH = 12 + 1.01 = 13.01

It is evident that the molecular weight 78.6 is 78.6/13.01 = 6 times the weight of the empirical formula. Hence the real formula of the compound is $(CH)_6$ i.e. C_6H_6.

Problem 4 : 1.36 litre of a gaseous compound weighs 2.62 gram at 22°C and 740 mm pressure. Find out its molecular weight.

Combining Charle's Law and Boyle's Law we have $P_1V_1/T_1 = P_2V_2/T_2$

P_1 = 740 mm of mercury ; P_2 = 760 mm of mercury
V_1 = 1.36 litre ; V_2 = ?
T_1 = 273 + 22 = 295°K ; T_2 = 273°K

Hence $(740\times1.36)/295 = (760\times V_2)/273$
Therefore V_2 = 1.23 litre = 1230 ml
Standard density = 2.62/1230 = 0.0021 gram/ml

Relative density or vapour density = standard density of the gas/
standard density of hydrogen
= 0.0021/0.00009 = 23.3

Therefore the molecular weight = 2×vapour density = 2×23.3 = 46.6

Problem 5 : The specific heat of an element is 0.082 Cal/g°C. Its gram equivalent weight is 23.24. Find out its correct gram-atomic weight.

Following Dulong and Petit's Law we write :

$$\text{specific heat} \times \text{gram atomic weight} \simeq 6 \text{ Cal/°C}$$

$$\text{gram atomic weight} = 6/0.082 = 73 \text{ gram}$$

$$\text{gram atomic weight} = \text{gram equivalent weight} \times \text{valence}$$

$$\text{Hence valence} = 73/23.24 = 3.1$$

Valence has to be an integer ; hence the correct valence is 3. Therefore the correct atomic weight is given by $23.24 \times 3 = 69.72$.

Problem 6 : 1 gram of calcium chloride is reacted with enough sodium sulphate to give a precipitate of 1.225 gram calcium sulphate. Calculate the equivalent weight of calcium (equivalent weights : Cl^- : 35.5 ; SO_4^{2-} : 48).

The following double decomposition reaction takes place :

$$CaCl_2 + Na_2SO_4 \rightarrow CaSO_4 + 2NaCl$$

The chloride and the sulphate ions are monovalent and bivalent respectively. Let us assume that the gram atomic weight of calcium is x.

$$\text{Molecular weight of } CaCl_2 = x + 2 \times 35.5 = x + 71.0$$

$$\text{Molecular weight of } CaSO_4 = x + 2 \times 48 = x + 96$$

$$\text{The ratio } \frac{CaCl_2}{CaSO_4} = \frac{1}{1.225}$$

$$\text{Therefore } \frac{x + 71}{x + 96} = \frac{1}{1.225} \; ; \; (x + 71) \times 1.225 = (x + 96) \times 1$$

$$\text{Hence } 0.225x = 96 - (71 \times 1.225) = 9.03$$

$$x = 9.03/0.225 = 40.1$$

Since calcium is bipositive its equivalent weight is half its atomic weight. So the equivalent weight comes out to be 20.05.

11.7. DETERMINATION OF MOLECULAR WEIGHTS

11.7.1. Molecular Weight : *Molecular weight of a compound is a number that indicates how heavy a molecule of the compound is compared to 1/12th of a carbon-12 atom.* Thus the statement that H_2O has a molecular weight 18 means that one molecule of H_2O is 18 times heavier compared to 1/12th of a carbon-12 atom. *Gram molecular weight of a compound is that weight of the compound in gram that contains the same number of molecules as the number of atoms contained in 12 grams of carbon-12.* It is the molecular weight of the compound in *amu* but expressed as grams. Thus the molecular weight of H_2O in *amu* is 18. Gram molecular weight is 18 gram.

11.7.2. Determination of Molecular Weights by Vapour Density Method : It is possible to determine the density of a gaseous compound experimentally. We can then express that relative to the density of hydrogen. We have already seen that the vapour density thus obtained is half the molecular weight of the compound. Again one of Avogadro's contributions to science states that *one gram mole of a gaseous substance occupies at standard temperature and pressure* 22.4 *litres.* So compared to hydrogen we can write the following for the vapour density of a gaseous compound :

$$\text{Vapour density} = \frac{\text{mass of 22.4 litres at S.T.P. of the compound}}{\text{mass of 22.4 litres of hydrogen at S.T.P}}$$

$$= \frac{\text{mass of one gram mole of the compound}}{\text{mass of one gram mole of hydrogen}}$$

$$= \frac{\text{mass of one gram mole of the compound}}{2}$$

Thus gram molecular weight of a gaseous compound = 2 × vapour density

11.7.2. Determination of Molecular Weights of Volatile Liquid Compounds : For such determination we can profitably utilise Avogadro's enunciation that one gram mole of a gaseous compound occupies 22.4 litres at S.T.P. Usually such determinations are made by the Victor Meyer's method. A small amount of a volatile liquid is taken in a thin walled glass ampule and sealed. By noting down the initial and final weights the weight of the liquid is recorded. This ampule is then dropped down into a Victor Meyer's apparatus which is being heated in an outer copper jacket. The ampule breaks and the liquid volatilises and moves up the column of the tube. The air thus displaced is collected through a side tube into a gas burette by displacement of water. The prevailing pressure (corrected for the aqueous tension at the temperature of collection)and the temperature are recorded.

weight of the sample = w gram ; standard volume = v' ml
volume of the sample = v ml ; standard temperature = 273°K
temperature = t°C ; standard pressure = 760 mm
pressure = p mm

$$\text{Then } v' = \frac{273\,pv}{(273+t)\,760}\ \text{ml.}$$

We recall that one gram mole at S.T.P. occupies 22.4 litres.

$$\text{Molecular weight} = \frac{w \times 22{,}400 \times (273+t) \times 760}{273\,pv}\ \text{gram}$$

11.7.3. Determination of Molecular Weights by Elevation of Boiling Point and Depression of Freezing Point : When a solute is dissolved in a solvent to produce a solution of known concentration, then the boiling point of the solution is found to be elevated while the freezing point is lowered compared to the boiling point and the freezing point of the pure solvent. The magnitude of the elevation or the depression is dictated by a constant characteristic of the solvent, molecular weight of the solute and of course by the concentration of the solute in the solvent. The following proportionality exists :

$$\left| T - T_1 \right| \propto \frac{1}{M}$$

where T is boiling point or the freezing point of the pure solvent, T_1 stands for the same of the solution and M represents the molecular weight of the solute. Specifically we can write :

$$\triangle T = K \frac{1000\ w_2}{M\ w_1}$$

where $\triangle T$ is the elevation or depression, K is the characteristic constant of the solvent, w_2 and w_1 are the weights of the solute and the solvent respectively and M is the molecular weight. It can be appreciated that 1000 w_2/Mw_1 is the *molality of the solution* i.e. *number of moles of the solute dissolved per* 1000 *gram of the solvent.*

Table 11.2 records the constant K for some commonly used solvents.

Table 11.2. Freezing Point Depression and Elevation of Boiling Point Constants of some Solvents

Solvent	Freezing Point Constant	Boiling Point Constant
Water	1.86	0.54
Acetic acid	3.90	3.07
Benzene	5.10	3.27
Nitrobenzene	6.90	—
Chloroform	3.88	2.60
Acetone	1.67	2.23

EXERCISES

1. Explain the terms atomic weight and molecular weight.

2. Is it possible to use any absolute standard unit for atomic weight and molecular weight?

3. What is vapour density? How can we get at the molecular weights of volatile substances from vapour density?

4. State Dulong and Petit's Law. Explain how this Law along with a knowledge of the valence can give us an accurate estimate of the atomic weight of a metallic element.

5. What is isomorphism? How can we use isomorphism to evaluate the atomic weight of an element?

6. State how we can arrive at the molecular weight of a compound following Avogadro's hypothesis.

CHAPTER 12

DETERMINATION OF THE STRUCTURES OF CHEMICAL COMPOUNDS

12.1. INTRODUCTION

With the advancement of knowledge in physics and chemistry the one vexing problem was the internal structure of chemical compounds. In a polyatomic compound the interrelations among the different atoms posed a paramount problem. For example it was a natural question to ask whether a compound ML_2 has a linear or a triangular arrangement of the constituents. Similarly a compound of composition ML_4 could admit of a tetrahedral or a square planar geometry. Sustained theoretical and experimental researches of a varied sort had to be undertaken over many many years to arrive at the correct answers. Today chemists and physicists can draw upon a very large number of complementary techniques to unfold the structure of even a very complex molecule. In this elementary book we shall deal with only a few simple techniques in their outline so as to provide the young readers with a peripheral idea of the actual field. The methods that will be touched upon are : (*a*) spectroscopy (*b*) X-ray diffraction (*c*) magnetic moment (*d*) dipole moment and (*e*) molecular conductivity

12.2. SPECTROSCOPY

In modern times a variety of spectroscopic techniques are available for investigating the structures of chemical compounds. Of these we will discuss in brief only the infrared spectroscopy and inorganic electronic spectroscopy.

12.2.1. Infrared Spectroscopy : In the simplest form a molecule may be visualised as an assemblage of atoms. These atoms may, in turn, be viewed as balls of different masses. These balls are held together by chemical bonds, which may be viewed as springs. These balls are under constant motion about the bond axis. A major motion or vibration is *stretching* during which the distance between the atoms decreases or increases but they are stationed along the same bond axis. A second type of vibration relates to *bending* or *deformation* during which the position of the atoms changes with respect to the original bond axis. Such stretching or bending vibrations take place at certain fixed energies i.e. at certain fixed frequencies. When the molecule is excited by infrared light of that same frequency then energy is absorbed and the amplitude of vibration is increased. Usually the sample is mixed with KBr and made into a thin transparent pellet under high pressure and the pellet is then exposed to infrared light of varying frequencies. Depending on the nature of the constituent atoms and the chemical bonds energies of different frequencies are absorbed. Typical radicals or bonds have typical frequencies of absorptions (Fig. 12.1).

The stretching frequency $\bar{v}$ is, as can be guessed, dependent on (*a*) the masses of the two atoms (M_x and M_y) (*b*) velocity of light *c* and (*c*) the force constant, *k*, of the bond. The relation is given by :

$$\bar{v} = \frac{1}{2\pi c}\left(\frac{k}{M_X M_y/(M_X + M_y)}\right)^{\frac{1}{2}} .$$

The masses are expressed in gram while the force constant is given in dynes/cm. It is interesting to note that in Chapter 5 we have said that the bond strength increases with increasing multiplicity of the bond. It is seen that the force constant as calculated from the experimental frequency reveals that it varies as 5, 10 and 15 × 10^5 dynes/cm with single, double and triple bonds respectively. In Table 12.1 the wave length as well as the frequency of certain absorption are given. Remember as wave length ($\mu = 10^{-4}$ cm) decreases frequency increases.

Table 12.1. Infrared Absorptions of Some Selected Functional Groups

Group	Wave Length (μ)	Wave Number (cm^{-1})
$>C=O$	5.80 – 5.87	1725 – 1705
$-COOH$ $(C=O)$	5.80 – 5.88	1725 – 1700
$N-H$ (primary amine)	2.86	3500
$-C\equiv N$ (nitrile)	4.42 – 4.46	2260 – 2240
$>C=N$ (imine, oxime)	5.92 – 6.10	1690 – 1640
$>S=O$ (sulphoxide)	9.35 – 9.71	1070 – 1030
$-S-H$ (mercapto)	3.85 – 3.92	2600 – 2550

12.2.2. Inorganic Electronic Spectroscopy : Most inorganic transition metal compounds absorb in the visible region of the spectrum and thereby furnish valuable information about the internal geometry of the molecule. Light can be broadly classified into three ranges :

ultraviolet region : 200 – 400 nm ;
visible region : 400 – 800 nm ;
infrared region : 2 – 16μ ;
(nm = nanometer = millimicron = mμ
= 10A = 10×10^{-8}cm = 10^{-7} cm; $\mu = 10^{-4}$cm;)

Measurement of the absorption spectrum of coordination complexes has helped a lot to predict their structures. The subject has grown over the past two decades to an enormous extent. For our present purpose we will discuss the simplest possible case of the complex $[Ti(H_2O)_6]\ Cl_3$. We can guess that titanium (III) is surrounded by the six monodentate H_2O molecules in an octahedral array. The six lone pairs of electrons of the six H_2O molecules are situated at the six corners of a regular octahedron i.e. they are stationed on either side of the three cartesian axes (x,y and z). Titanium (III) has a single $3d$ electron. The five $3d$ orbitals have different orientations in space (Fig. 12.2). Only two orbitals, namely $d_{x^2-y^2}$ and d_{z^2} have their lobes along the cartesian axes while the other three, namely d_{xy}, d_{xz} and d_{yz}, have their lobes in between the cartesian axes. We can guess that the titanium electron will take up a position in one of these five d orbitals such that it is energetically stable. Electrons in the two orbitals $d_{x^2-y^2}$ and d_{z^2} will be heavily repelled by the ligand lone pairs because they are situated right on the cartesian axes facing the ligand lone pair electrons. On the other hand electron in any of the remaining three orbitals will be repelled less i.e. will be comparatively stabilised. In essence there will be a splitting of the otherwise equienergetic (i.e. degenerate) d orbitals in two levels (Fig. 12.3). The single d electron of titanium (III) will occupy the lower energy set (d_{xy}, d_{xz} and d_{yz}). If this electron is supplied the energy equal to the difference between the two sets of orbitals (i.e. lower triplet and upper doublet) then it will be excited and will move over to the upper doublet set. While doing so it will absorb energy from white light corresponding to the energy difference mentioned above and will transmit the complementary colour. Actual measurement in a spectrophotometer shows that hexaaquo titanium (III) ion absorbs at 550 nm giving a single absorption band as demanded by the simple reasoning developed

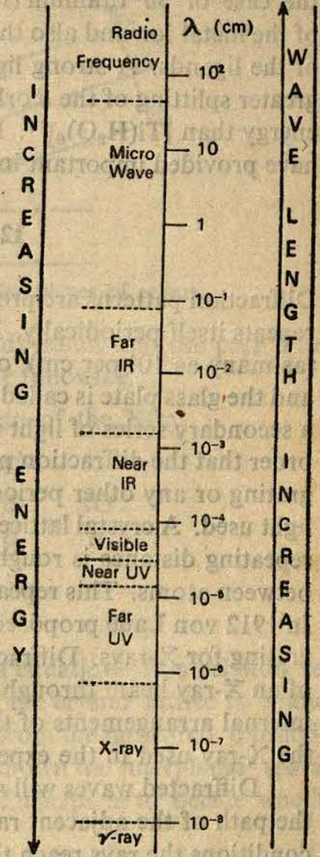


Fig. 12.1. Wavelengths of various types of radiation

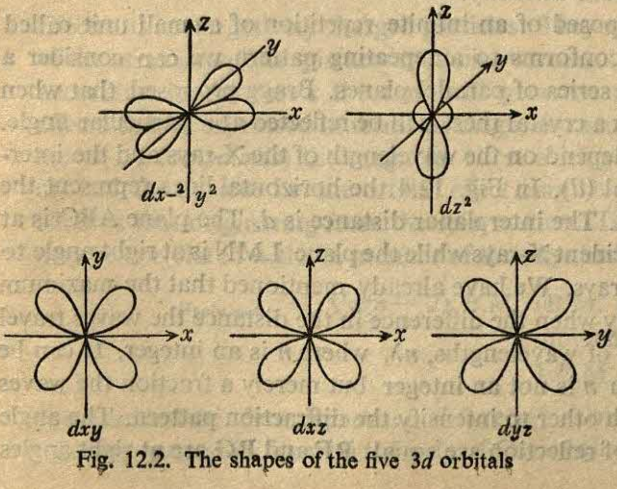


Fig. 12.2. The shapes of the five $3d$ orbitals

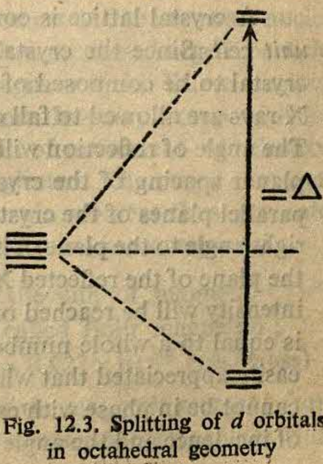


Fig. 12.3. Splitting of d orbitals in octahedral geometry

above. We see the complex violet because of the complementary colour. It may be pointed out here that the nature of the absorption spectrum (a single band in the case of $3d^1$ titanium (III)) will vary depending on the number of *d* electrons of the metal ion and also the energies of absorption will be dictated by the nature of the ligands. A strong ligand will have a greater repelling effect and hence a greater splitting of the *d* orbitals. Thus $[Ti(dipyridyl)_3]^{3+}$ will absorb at a higher energy than $[Ti(H_2O)_6]^{3+}$. In essence studies of the electronic spectra of complexes have provided important information about the stereochemistry.

12.3. X-RAY DIFFRACTION

Diffraction patterns are produced whenever light passes through a structure which repeats itself periodically. For example, it is possible to draw closely spaced lines (as many as 10^4 per cm) on a glass plate. Each such line is at 10^{-4} cm apart and the glass plate is called a *grating*. When a beam of light strikes such a grating a secondary series of light waves emanate giving rise to a diffraction pattern. In order that the diffraction pattern may be prominent, the repeating distance of the grating or any other periodic structure should be close to the wavelength of the light used. A crystal lattice is a three dimensional repeating structure in which the repeating distance is roughly of the order of 10^{-8} cm. This is also the distance between atoms. This repeat distance is of the order of the wave length of X-rays. In 1912 von Laue proposed that it will be possible for a crystal lattice to act as a grating for X-rays. Diffraction patterns should thus be produced by the passage of an X-ray beam through a crystal and the diffraction pattern should reflect the internal arrangements of the atoms in the crystal and also of the wavelength of the X-ray used in the experiment.

Diffracted waves will show a maximum intensity only when the difference in the path of the adjacent rays is an integral number of wavelengths. Under such conditions the rays reach the detector *in phase*. On the other hand when the rays do not travel integral number of wavelengths before meeting they are *out of phase* and cannot produce maximum intensity.

A crystal lattice is composed of an infinite repetition of a small unit called *unit cell*. Since the crystal conforms to a repeating pattern we can consider a crystal to be composed of a series of parallel planes. Bragg proposed that when X-rays are allowed to fall on a crystal these will be reflected at a particular angle. The angle of reflection will depend on the wavelength of the X-rays and the interplanar spacing of the crystal (*d*). In Fig. 12.4 the horizontal lines represent the parallel planes of the crystal. The interplanar distance is *d*. The plane ABC is at right angle to the plane of incident X-rays while the plane LMN is at right angle to the plane of the reflected X-rays. We have already mentioned that the maximum intensity will be reached only when the difference in the distance the waves travel is equal to a whole number of wavelengths, $n\lambda$, where n is an integer. It can be easily appreciated that when n is not an integer but merely a fraction the waves cannot be in phase with each other to intensify the diffraction pattern. The angle of incidence and the angle of reflection are equal. RF and RG are at right angles to the angles of incidence and reflection respectively. It is observed from the figure that the path BSM is greater than the path ARL and that the extra length

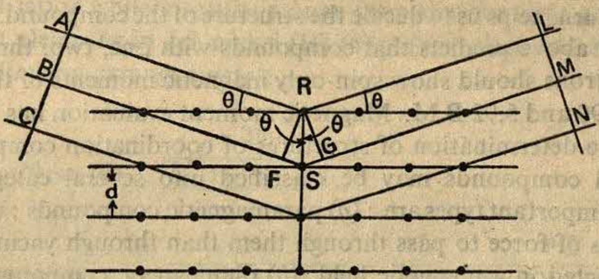


Fig. 12. 4. Differaction of X-rays from successive planes of atoms

of BSM is equal to the sum of FS and SG. We already know that the path difference for the two waves is $n\lambda$, so that we can write the following :

$$\mathrm{FS} + \mathrm{SG} = n\lambda \quad (\lambda = \text{wavelength of the X-ray ;}$$

$$n = \text{an integer})$$

$$\text{Again } \sin\theta = \frac{\mathrm{FS}}{\mathrm{RS}} = \frac{\mathrm{SG}}{\mathrm{RS}} = \frac{\mathrm{FS}}{d} = \frac{\mathrm{SG}}{d}$$

$$\text{Therefore} \quad \mathrm{FS} = \mathrm{SG} = d\sin\theta$$

$$\text{So we have} \quad n\lambda = 2d\sin\theta$$

The above equation is the famous Bragg diffraction equation. This relation tells us that if the interplanar spacing *d* of the planes of the crystal lattice is known, then the wavelength of the X-rays can be calculated from the measured diffraction angle θ. On the contrary if the X-ray wavelength is known the interplanar spacing of a particular crystal can be evaluated. Knowledge of *d* helps us to decide whether or not two crystals are isomorphous.

12.4. MAGNETIC MOMENT

Electrons are negatively charged particles. They move around the central nucleus of the atom as well as spin around their own axes. Movement of charged particles, according to Ampere's theorem will generate magnetic field. These magnetic effects can be expressed in terms of magnetic moments. In many compounds (*but not in all compounds*) the magnetic effect arising out of movement of electrons around the nucleus i.e. the orbital effect may be neglected. The major magnetic effect is that originating from the spin motion. The spin moment thus generated may be correlated with the number of the unpaired electrons in a compound :

$$\mu_{\text{spin-only}} = \sqrt{n(n+2)}\ \text{B.M.} \quad (\text{B.M. is the unit of magnetic moment called Bohr magneton ; } 1\ \text{B.M.} = 0.927\times10^{-20}\ \text{ergs/gauss})$$

From an independent experimental determination of the magnetic moment from magnetic susceptibility with the help of Curie equation one can compare the value with the theoretically predicted value for a given number of unpaired electrons. Such evaluation tells us how many unpaired electrons the compound really has. This, in turn, helps us to decide the structure of the compound. The theoretical relation given above predicts that compounds with one, two, three, four or five unpaired electrons should show spin-only magnetic moments of the order of 1.73, 2.83, 3.87, 4.90 and 5.92 B.M. Magnetic moment evaluation has been an invaluable aid in the determination of structures of coordination compounds.

Chemical compounds may be classified into several categories. Of these the two most important types are : (*a*) paramagnetic compounds : these allow more magnetic lines of force to pass through them than through vacuum. As a result they are attracted in a magnetic field, (*b*) diamagnetic compounds : these allow lesser number of lines of force to pass through them than through vacuum. As a consequence they are repelled by a magnetic field. It is observed that compounds with all electrons paired are diamagnetic while compounds with one or more unpaired electrons have their spins unneutralised and hence they show paramagnetic behaviour.

A given chemical compound is subjected to a magnetic field. Usually a glass tube is filled with the sample under examination and is suspended from an arm of a sensitive chemical balance into a magnetic field. In the case of a paramagnetic body more lines of force will tend to pass through the body. As a consequence the sample will be dragged into the strongest part of the magnetic field and there will be an apparent increase in its mass. The apparent increase in mass multiplied by the acceleration due to gravity will give the force acting on the sample. Such an examination of the sample gives us a measure of its susceptibility towards magnetisation. The susceptibility (χ_M) of the sample is expressed by the following relation :

$$\chi_M = \frac{2l \times \left(\begin{array}{c}\text{difference in mass before and after application of} \\ \text{magnetic field} \times g\end{array} \right) \times M}{H^2 \times \text{mass of the sample}}$$

(M = molecular weight ; g = acceleration due to gravity ; H = strength of the magnetic field)

The susceptibility is then converted to the moment via Curie equation :

$$\chi_M = \frac{N\mu^2}{3kT} \quad (N = \text{Avogadro number} ;\ k = \text{Boltzmann constant};\ T = \text{absolute temperature})$$

The magnetic moment, determined experimentally, is then compared with the spin magnetic moment formula derived theoretically ($\mu = \sqrt{n(n+2)}$B.M.) to ascertain how many unpaired electrons the system has.

We will now take an example to demonstrate how such magnetic studies help reveal the internal structure of a coordination complex. In the chemical laboratory bivalent nickel is tested by dimethylglyoxime when a rose-red precipitate separates. The ligand (Chapter 6 ; Fig. 3) is bidentate. Hence coordination number of nickel (II) in bis (dimethylglyoximato) nickel (II) is four. With such a coordination number the complex may be either tetrahedral or square planar (Tables 5.2 and 6.1). In order to have a tetrahedral geometry nickel (II) has to have sp^3 hybridisation while a square planar geometry requires a dsp^2 hybridisation. The eight electrons in $3d^8$ nickel (II) (all other electrons are paired) will assume the following arrangements :

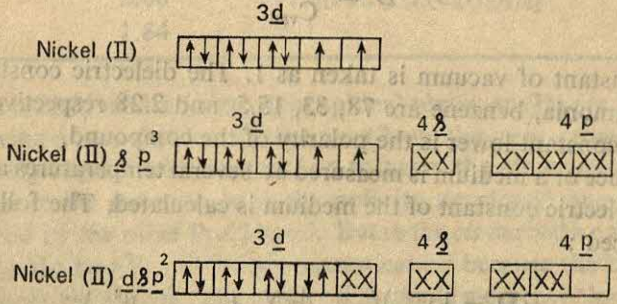


Fig. 12.5. Electron arrangements in $3d^8$ nickel (II) in sp^3 tetrahedral and dsp^2 square planar geometries. The crosses stand for the ligand lone pairs occupying the hybrid orbitals of the nickel (II).

The $3d$ orbitals remaining after allowing for the ligand lone pairs are used to accommodate the nickel (II) electrons. Fig. 12.5 tells us that if the geometry is tetrahedral then there should be left two unpaired electrons giving a spin moment of $\sqrt{2(2+2)} = 2.83$ B.M. but in the case of a square planar geometry there should remain no unpaired electron. Hence the substance should behave as a diamagnetic compound. Experiments show that the complex is diamagnetic. Thus we see that magnetic measurement settles the geometry of this complex. This is one of many many compounds whose structures have been settled through magnetic studies.

12.5. DIPOLE MOMENT

When a covalent compound is formed out of two elements of different electronegativities, the compound may show polarity depending on its geometry. Thus H_2O is a polar molecule. The two bonds are polar and the molecule shows a resultant polarity. When the extra charge at one end of the molecule is δ^+ (or δ^-) and the distance between the positive and the negative centres is d the molecule has a dipole moment $\mu = \delta d$. In some cases the individual bonds may be polar but the resultant of the polar bonds may be zero. In such situation the molecule will be non-polar although there is an electronegativity difference between the combining elements. Examples of such non-polar molecules are CCl_4, BeF_2.

Capacitance of a condenser may be defined as :

$$C = \frac{\text{charge on one plate}}{\text{potential difference between the two plates}}$$

Capacitance depends on the material between the plates. Capacitance will decrease if the medium between the two plates is filled with a non-conductor instead of vacuum. The ratio of the capacitance in a medium x to the capacitance in vacuum is called the dielectric constant (D) of the medium :

$$D = \frac{C_X}{C_{vac}}$$

Dielectric constant of vacuum is taken as 1. The dielectric constants of water, methanol, ammonia, benzene are 78, 33, 15.5 and 2.28 respectively. The lower the dielectric constant lower is the polarity of the compound.

Capacitance of a medium is measured at several temperatures and from these results the dielectric constant of the medium is calculated. The following relation can be deduced :

$$\left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4\pi N}{3}\left(\alpha_D + \frac{\mu^2}{3kT}\right)$$

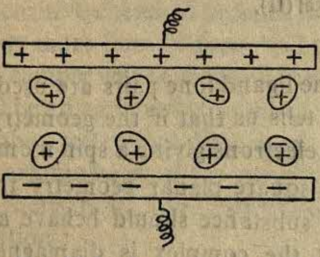


Fig. 12.5. A condenser with dipolar substance

where M = molecular weight of the substance

ρ = density

N = Avogadro number

K = Boltzmann constant

T = Absolute temperature

μ = Dipole moment

α_D = Dipole moment induced on the medium by the electric field

The above equation may be expressed more simply by :

$$y = A + B(1/T) \text{ where } y = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho}\ ;\ A = \frac{4\pi N}{3}\alpha_D\ ;$$

$$\text{and } B = \frac{4\pi N}{3}\,\frac{\mu^2}{3k} = \frac{4\pi N\mu^2}{9k}$$

These experiments are conducted at several temperatures. Thereafter a plot of y against $1/T$ is made. The slope of this plot will furnish the value of B wherefrom the dipole moment, μ, can be had.

When an electronic charge is separated from a similar positive charge by a distance of 1A then the dipole moment, μ, will be given by 4.8×10^{-10} esu $\times 10^{-8}$ cm $= 4.8\times10^{-18}$ esu cm $= 4.8$ Debye units. The unit of dipole moment is 1 Debye = D = 10^{-18} esu cm.

Table 12.2 records dipole moments of some representative compounds.

Table 12.2 Dipole Moments of Some Compounds (in Debye units)

Compound	Dipole	Compound	Dipole
H_2	0	CCl_4	0
Cl_2	0	*trans*$[PtCl_2\{P(C_2H_5)_3\}_2]$	0
HF	2.00	*cis*$[PtCl_2\{P(C_2H_5)_3\}_2]$	10.7
H_2O	1.84		

The *cis* and *trans* dichloro bis (triethylphosphine) platinum (II) are isomeric. The one isomer having a zero dipole moment must have the *trans* structure while the one having a very high dipole moment has to have the *cis* structure. It can be appreciated that in the *trans* structure the polarity developed due to one Pt-Cl bond is cancelled by the other Pt-Cl bond. But in the *cis* derivative the two dipole moments due to the two Pt—Cl bonds cannot cancel because the bonds are not directed opposite to each other. Thus we see that dipole moment helps us to identify the *cis-trans* isomers in four coordinate platinum (II) complexes. Furthermore the identification of the two isomers tells us that the complexes cannot have a tetrahedral geometry because a tetrahedral MA_2B_2 cannot admit of any isomers. In a tetrahedron the two A and the two B groups are equidisposed around M and hence cannot exhibit any isomerism.

12.5. MOLECULAR CONDUCTIVITY

Molecular conductivity of a simple or a complex compound can give us important informations about its ionic nature and any solvolysis or ion-pairing. In the case of a coordination complex such measurements help us to decide whether an anionic ligand is inside or outside the coordination zone. The following relation is used in calculating the molecular conductivity of a compound :

$$\Lambda_M = \frac{k \times 1000}{c \times \text{resistance of the solution}}$$

where k is the cell constant and c is the molar concentration.

Table 12.3. records molecular conductivity of some electrolytes in aqueous medium.

Table 12.3. Molecular Conductivity of Some Electrolytes in Aqueous Medium

Charge type	Concentration of measurement	Molecular Conductivity ($ohms^{-1}\ cm^2\ mole^{-1}$)
1 : 1 (two ions)	0.001 *M*	95 – 115
2 : 1 (three ions)	0.001 *M*	222 – 265
3 : 1 (four ions)	0.001 *M*	380 – 430
4 : 1 (five ions)	0.001 *M*	~520

The molecular conductivities of $[Co(NH_3)_6]Cl_3$, $[Co(en)_2Cl_2]$ Cl and $[Pt(NH_3)_2Cl_2]$ (*cis*) are 432, 97 and 5 ohms^{-1} cm^2 mole^{-1} respectively. These values identify these complexes as 3 : 1, 1 : 1 and a non-electrolyte respectively. The non-electrolytic nature of *cis* $[Pt(NH_3)_2Cl_2]$ also tells us that the two chloride groups are attached to the platinum (II).

EXERCISES

1. Give a resume of some simpler methods of determination of structures of chemical compounds.

2. Give a qualitative description of the principles of infra-red spectra. How do such spectra assist us in ascertaining the presence or absence of typical functional groups in an organic molecule?

3. What is the difference between a diamagnetic and a paramagnetic substance ? Explain with one example how magnetic measurements help us in arriving at the geometry of a particular complex.

4. Calculate the spin moment of chromium (III) and vanadium (III) compounds.

5. What is dipole moment? Explain with the help of examples how dipole moment determination helps us in drawing conclusions about the structures of compounds.

6. Explain which of the following compounds are expected to have dipole moments :

BeF_2 ; CCl_4 ; NF_3 ; H_2O ; *cis/trans* $[Pt(NH_3)_2Cl_2]$;

CHAPTER 13

A SURVEY OF METAL EXTRACTION PROCEDURES

13.1. INTRODUCTION

We are almost ready to explore the chemistry of the chemical elements. An important aspect of the metal chemistry is their extraction from natural sources. In this Chapter we propose to make a general survey of the extraction procedures and the background that leads to a particular method for a particular metal.

In nature almost all the elements exist in the form of some chemical combination. Gold is one notable exception which is found *native* in nature. The alkali and the alkaline earths mainly occur as halides and sulphates : NaCl ; KCl, $MgCl_2.6H_2O$; CaF_2 ; $CaSO_4$ etc. The alkaline earths are also found in the form of their carbonates and phosphates: $CaCO_3$; $Ca_3(PO_4)_2$; $SrCO_3$ etc. Aluminium, iron, chromium and manganese occur primarily as their oxides: $Al_2O_3.2H_2O$; Fe_2O_3 ; Cr_2O_3 ; MnO_2 ; $FeO.Cr_2O_3$. Lead, mercury and copper are found mostly as their sulphides : PbS ; HgS ; $CuFeS_2$ etc.

13.2. STANDARD REDUCTION POTENTIALS

We have already noted in Chapter 7 that a negative reduction potential means that the metal has a ready tendency to give up its outer electrons to form corresponding metal ions. The more negative the potential value the more easily does the element form the cation. Conversely it becomes difficult to reduce a metal ion with negative reduction potential back to the metallic state. In the entire periodic table the alkalies and the alkaline earths have considerably negative reduction potentials for the conversion $M^{n+} + ne \rightleftharpoons M$. The most powerful method of reduction has to be employed for the reduction of these metal ions back to their elementary states. It is an experimental fact that one has to take recourse to electrolytic reduction, the most powerful reduction method, for those metal ions whose reduction potentials range from -3.04 volts to -1.5 volts (Table 13.1).

It is possible to reduce the metal ions whose reduction potentials are within the range -1.5 to -0.75 volts by metals having a still more negative potential. For example aluminium ($Al^{3+} + 3e \rightleftharpoons Al$; $E^\circ = -1.66$ volts) is employed for reduction of oxides of iron, chromium, manganese. This is the well known Goldschmidt alumino-thermite reduction method.

Carbon, a comparatively less effective reducing agent, is pressed to service when reduction of metal oxides, with low negative reduction potentials (from 0.00 volts to -0.75 volts), is called for.

Oxides or sulphides of the metals whose reduction potentials are positive (i.e. which metals are even less electropositive compared to hydrogen) can often be decomposed to the metallic state just by the application of heat. HgO serves as a good example.

Figure 13.1 depicts what we have so far tried to make out with regard to the reduction potentials and the metal extraction procedures.

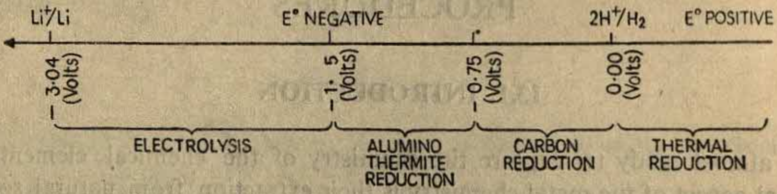


Fig. 13.1. Standard reduction potentials and metal extraction procedures

One should not assume from the tone of the above discussion that electrolytic procedure cannot be extended to metals outside the range of the reduction potentials −3.04 volts to −1.50 volts. In fact what we have tried to point out is that the electrolytic reduction is the most powerful reduction method known so far and it can surely be extended to compounds of other metals provided we get compounds which behave as either good electrolytes in their fused state or in aqueous solution. It is indeed a fact that we do make use of the electrolytic procedure during purification of the elements like zinc ($E^\circ = -0.76$ volts), copper ($E^\circ = +0.337$ volts), silver ($E^\circ = +0.799$ volts) etc. (Table 13.2). The prowess of the several reduction procedures varies in the following order :

electrolysis > aluminium reduction > carbon reduction > thermal decomposition

Table 13.1. Reduction Potentials and Electrolytic Procedures of Metal Extraction.

Metal	Reduction Potential $M^{n+} + ne \rightleftharpoons M$ (volts)	Electrolyte	Cathode (*a*)	Anode (*b*)	Reactions at the electrodes
Li	−3.04	fused LiCl	Iron	Carbon	(*a*) $Li^+ + e \rightarrow Li$ (*b*) $2Cl^- \rightarrow Cl_2 + 2e$
Na	−2.71	fused NaCl (KCl + KF)	Iron	Carbon	(*a*) $Na^+ + e \rightarrow Na$ (*b*) $2Cl^- \rightarrow Cl_2 + 2e$
Mg	−2.37	fused $MgCl_2$	Steel	Carbon	(*a*) $Mg^{2+} + 2e \rightarrow Mg$ (*b*) $2Cl^- \rightarrow Cl_2 + 2e$
Ca	−2.87	fused $CaCl_2$ (CaF_2)	Iron	Carbon	(*a*) $Ca^{2+} + 2e \rightarrow Ca$ (*b*) $2Cl^- \rightarrow Cl_2 + 2e$
Al	−1.66	Al_2O_3 (Na_3AlF_6)	Iron	Carbon	(*a*) $2Al^{3+} + 6e \rightarrow 2Al$ (*b*) $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e$

Table 13.2. **Standard Potentials and Electrolytic Refining**

Metal	Reduction Potential $M^{n+} + ne \rightleftharpoons M$ (volts)	Electrolyte	Cathode (*a*)	Anode (*b*)	Reactions at the electrodes
Zn	-0.76	$ZnSO_4$ dil. H_2SO_4	Pure zinc	Impure zinc	(*a*) $Zn^{2+} + 2e \rightarrow Zn$ (*b*) $Zn \rightarrow Zn^{2+} + 2e$
Cu	0.337	$CuSO_4$ dil. H_2SO_4	Pure copper	Impure copper	(*a*) $Cu^{2+} + 2e \rightarrow Cu$ (*b*) $Cu \rightarrow Cu^{2+} + 2e$
Ag	0.799	Aqueous $AgNO_3$	Pure silver	Impure silver	(*a*) $Ag^{+} + e \rightarrow Ag$ (*b*) $Ag \rightarrow Ag^{+} + e$
Au	1.68	Aqueous $Na[Au(CN)_2]$	Pure gold	Impure gold	(*a*) $Au^{+} + e \rightarrow Au$ (*b*) $Au \rightarrow Au^{+} + e$

13.3. REDUCTION BY METALS

Aluminium is the most used metal in the reduction of some selected metal oxides. Magnesium has been used in fewer special cases. The standard reduction potential of $Al^{3+} + 3e \rightleftharpoons Al$ is -1.66 volts. This negative potential indicates that this metal will serve as a reductant of those metal oxides, when E° values of the corresponding metals are less negative than -1.66 volts. For example the E° value for $Cr^{3+} + 3e \rightleftharpoons Cr$ is -0.74 volts. Hence aluminium will be satisfactory reductant for reduction of Cr_2O_3 to the chromium metal. Goldschmidt alumino-thermite process has been successfully used in the reduction of the following oxides :

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$$
$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$$
$$3MnO_2 + 4Al \rightarrow 3\,Mn + 2Al_2O_3$$
$$3NiO + 2Al \rightarrow Al_2O_3 + 3Ni$$

Standard reduction potential of $Mg^{2+} + 2e \rightleftharpoons Mg$ is -2.37 volts. This shows that metallic magnesium is a superior reductant compared to metallic aluminium. It is used in the reduction of B_2O_3 and SiO_2 at elevated temperature :

$$B_2O_3 + 3Mg \rightarrow 3MgO + 2B$$
$$SiO_2 + 2Mg \rightarrow 2MgO + Si$$

Standard reduction potentials of Zn^{2+}/Zn and Cd^{2+}/Cd couples are -0.763 and -0.40 volts. It follows that metallic zinc is capable of reducing cadmium (II) ion to metallic cadmium. In fact when an aqueous solution of impure cadmium salt is agitated with powered zinc, zinc goes into solution as zinc (II) ions while pure metallic cadmium precipitates out :

$$Cd^{2+} + Zn \rightarrow Zn^{2+} + Cd\downarrow$$

13.4. CARBON REDUCTION

Carbon, in the form of coke, is in great demand in many metal extraction procedures. This reductant is obtained plenty in nature in the form of coal, which can by processed in coke-ovens to bring it into the very effective reductant form coke. Formation of the gaseous CO or CO_2 also helps keep the reduction rather clean. It is profusely used in the industrial preparations of the metals : tin, lead, bismuth, iron, cobalt, zinc, mercury etc. During these industrial scale reductions some undesirable products also are formed. In order to remove these undesirable products the ores are mixed with coke alongwith limestone ($CaCO_3$), fluorspar (CaF_2), silica (SiO_2), alumina (Al_2O_3) etc. so as to form slags like $CaSiO_3$, $Ca(AlO_2)_2$ etc. Depending on a density difference between the molten metal and the molten slag it is possible to draw out the molten metal leaving behind the undesirable slag. Some of the carbon reductions are cited below :

I. $SnO_2 + 2C \xrightarrow{1200°C} Sn + 2CO$

$CaCO_3$ and CaF_2 are used to facilitate the formation of slag.

II. Lead is recovered from galena by the following reaction :

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

Limestone, coke and scrap iron are used to facilitate reduction and formation of the slag :

$$PbO + CO \rightarrow Pb + CO_2$$

$$FeO + PbS + C \rightarrow Pb + FeS + CO \; ; \; CaO + SiO_2 \rightarrow CaSiO_3$$

The slag consits of calcium silicate $CaSiO_3$ and FeS (Chapter 18).

III. Carbon is also used in the reduction of bismuth ores to metallic bismuth (Chapter 19)

$$2Bi_2S_3 + 9O_2 \rightarrow 2Bi_2O_3 + 6SO_2$$

$$Bi_2O_3 + 3C \rightarrow 2Bi + 3CO$$

IV. Conversion of haematite (Fe_2O_3) to iron is a very complex reduction process. Commonly a mixture of the haematite ore, carbon and limestone in the ratio 12 : 5 : 3 is treated in a blast furnace (Chapter 23) when the following reactions take place :

$$2C + O_2 \rightarrow 2CO$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$CaO + Al_2O_3 \rightarrow Ca(AlO_2)_2$$

The slag consisting of $CaSiO_3$ and $Ca(AlO_2)_2$ floats on the surface of the molten iron and is removed. (Chapter 23).

V. Carbon reduction is also carried out during the extraction of zinc from zinc blende :

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$ZnO + C \xrightarrow{1200-1400°C} CO + \text{distilled zinc}$$

VI. Recovery of mercury from cinnabar also makes use of carbon (Chapter 25)

$$2HgS + 3O_2 \rightarrow 2HgO + 2SO_2$$

$$HgO + C \rightarrow Hg + CO \ ; \ 2HgO \rightarrow 2Hg + O_2$$

In the above examples there are several elements which are more electropositive than carbon. Carbon reduction of their oxides should not have been possible in these cases. Because of a favourable entropy change in the reaction :

$2MO\ (s) + C \rightarrow 2M$ (solid or gas) $+ CO_2$ and more so in the reaction :

$MO\ (s) + C \rightarrow M$ (solid or gas) $+ CO$

carbon reduction of these oxides becomes feasible as the temperature is increased. Carbon reduction of some metal oxides (eg : Cr_2O_3, TiO_2) cannot be carried out because the metals (eg : Cr, Ti) form stable carbide with carbon.

13.5. THERMAL DECOMPOSITION

There are a few elements in the perodic table whose reduction potentials are quite positive. These positive potentials indicate that the tendency of these elements to give up their electrons is less pronounced than that of hydrogen. In other words their metal ions are likely to be reduced very easily. Thus we find that the oxides of silver, mercury, palladium, platinum can be easily decomposed by applying heat :

$$Ag_2O \xrightarrow{250°C} 2Ag + \tfrac{1}{2}O_2 : E°,\ Ag^+ + e \rightleftharpoons Ag,\ 0.799 \text{ volts}$$

$$HgO \xrightarrow{\text{red heat}} Hg + \tfrac{1}{2}O_2 : E°,\ Hg^{2+} + 2e \rightleftharpoons Hg,\ 0.789 \text{ volts}$$

$$PdO \xrightarrow{\text{heat}} Pd + \tfrac{1}{2}O_2 : E°,\ Pd^{2+} + 2e \rightleftharpoons Pd,\ 0.987 \text{ volts}$$

$$PtO \xrightarrow{\text{heat}} Pt + \tfrac{1}{2}O_2 : E°,\ Pt^{2+} + 2e \rightleftharpoons Pt,\ 1.200 \text{ volts}$$

13.6. METAL EXTRACTION BY SUBSTITUTION

Cyanide is known to be the strongest coordinating ligand. As a result metal ions like Ag^+, Au^+, Zn^{2+} etc. form stable cyano complexes of the form $Na[Ag(CN)_2]$, $Na[Au(CN)_2]$, $Na_2[Zn(CN)_4]$. Of the three metals silver, gold and zinc the last has a negative reduction potential i.e. zinc metal will tend to release its valence electrons to solution far more readily than silver and gold. Therefore if a solution of the cyano complex of silver (I) or gold (I) is treated with powdered zinc it is likely that zinc will pass on to solution as zinc (II) ion and the zinc (II) ion will replace the silver (I) or gold (I) inside the complex. The silver (I) or gold (I) will then take up the released electron from zinc and will be precipitated as metallic silver or metallic gold. This is indeed what is done during the extraction of silver or gold.

I. $$Zn \rightarrow Zn^{2+} + 2e$$

$$2Na[Ag(CN)_2] + Zn^{2+} \rightarrow Na_2[Zn(CN)_4] + 2\ Ag^+$$

$$2\ Ag^+ + 2\ e \rightarrow 2Ag$$

II. $$Zn \rightarrow Zn^{2+} + 2e$$

$$2Na[Au(CN)_2] + Zn^{2+} \rightarrow Na_2[Zn(CN)_4] + 2Au^+$$

$$2Au^+ + 2e \rightarrow 2Au$$

13.7. POSITION OF HYDROGEN AS A REDUCTANT IN METAL EXTRACTION

It is a well known fact that hydrogen is a good reducing agent. Yet we seldom find hydrogen being used for industrial purpose reduction. Hydrogen is not quite readily available and has to be obtained from electrolysis of water or as by-product of other industrial preparations. Moreover at higher temperature in the presence of oxygen it is likely to cause explosion. On the other hand carbon is more easily obtained from nature. For these reasons hydrogen is not used for large-scale reductions. However for research-scale reduction of freshly prepared metal oxides pure electrolytic hydrogen is used whenever necessary.

13.8. OCCURRENCE OF ELEMENTS IN NATURE AND RELATIVE ABUNDANCE

Earth's crust extends from its surface to around seventy five miles inwards. The elements present in compound form in this crust have been analysed and their relative abundances have been calculated. The relative abundances of some of the elements are given below :

Oxygen	50%	Potassium	2.4%
Silicon	26	Magnesium	1.9
Aluminium	7.5	Hydrogen	0.9
Iron	4.7	Titanium	0.6
Calcium	4.7	Chlorine	0.2
Sodium	2.6	Phosphorus	0.1

Among the elements whose relative abundances are less than 0.1% are manganese, carbon, sulphur, barium, chromium, nitrogen, fluorine, zirconium, zinc, nickel, strontium, vanadium etc.

13.9. OCCURRENCE OF METALS IN NATURE : MINERALS AND ORES

Most of the elements occur in nature in the form of some chemical compound. In general the different compounds in which a particular element is found to exist in nature are called *minerals* of that element. It is however not economically suitable to extract an element from all the different forms it exists in nature. Those minerals from which the extraction of an element becomes commercially viable are called its *ores*. *Thus all ores are minerals but all minerals are not ores.*

Cinnabar, HgS, is the well known ore of mercury. In some parts of the world mercury is found to occur as tiemannite, HgSe (mercuric selenide), and coloredoite, HgTe (mercuric telluride). From commercial point of view only cinnabar is good enough for bulk-scale extraction of mercury. Thus cinnabar, coloredoite and tiemannite are all mercury minerals but cinnabar alone is the ore.

13.10. CONCENTRATION OF THE METALLIC ORES

The ores of a particular metal cannot be straightway processed for its extraction. The reason is simple enough. When the ore is taken out from within the earth's crust the ore is admixed with undesirable siliceous matter and other metal compounds. These admixed materials make the extraction procedure costly unless the crude ore is removed largely from the undesirable materials. The removal of the unwanted materials eventually leads to concentration of the ore and this makes the extraction procedure more economic and free from further complications. Concentration also makes the ore porous enough to respond properly to all subsequent chemical reactions.

There are three major concentration procedures : (*a*) froth floatation procedure (*b*) magnetic field technique and (*c*) shaking and treating with running water.

I. FROTH FLOATATION PROCEDURE : The crude ore is first finely ground in a mechanical grinder and is then suspended in a mixture of water and an immiscible oil or other liquid eg. pine oil, xanthate or cresilic acid. This entire mixture is then agitated with a current of air. This air current leads to the formation of froth. In general it is observed that the fine particles of the ore surface up with the froth while the undesirable earthen and other matter settle down. The froth along with the fine particles are removed and thus the crude ore is substantially enriched.

Froth floatation process is applied for enrichment of zinc blende (Chapter 25), haematite (Chapter 23), galena (Chapter 18) etc.

II. MAGNETIC FIELD TECHNIQUE : There are some ores which have magnetic properties while the accompanying undesirable materials have none. Under favourable circumstances the crude ore is finely ground in a crusher and is then allowed to travel over a belt attached to a magnetic field. As the crude ore containing the mixture of a magnetic and a non-magnetic material passes from one pole of the the magnetic field to another the magnetic material deposits on a platform close to the leaving pole while the non-magnetic field collects at a distance away from the pole piece. Thus a separation and hence concentration of the ore is achieved.

Haematite, Fe_2O_3, the most important ore of iron is first concentrated by froth floatation process and thereafter by the magnetic field technique. The ore is magnetic while the accompanying materials are not.

The major ore of tin is casseterite, SnO_2. It is usually admixed in nature with iron pyrites (FeS), iron tungstate ($FeWO_4$), manganese tungstate ($MnWO_4$). While SnO_2 is non-magnetic others are magnetic. It has been possible to enrich the tin ore by the magnetic field technique.

Pyrolusite MnO_2, the major ore of manganese, is non-magnetic while the accompanying iron oxides are magnetic. Once again magnetic method has been applied for enrichment of the pyrolusite ore.

III. SHAKING AND TREATING WITH RUNNING WATER : There is usually a difference in the densities of the ore and the accompanying undesirable materials. The finely ground crude material is taken in Wolfram's Table which consists of a big-sized metal sieve. The table is given good shaking while a current of water runs along the table through the crude ore material. Thus the crude material is simultaneously exposed to two effects : (*a*) shaking of the table and (*b*) agitation by running water. Depending on the density difference the earthy matter is usually carried away with the running water while the desired ore is left behind and is collected on the Wolfram's Table.

Finely ground chromite FeO. Cr_2O_3 and also finely ground cassiterite SnO_2 are substantially freed from silica and other lighter materials by this process.

13.11. SOME TECHNICAL TERMS IN EXTRACTION PROCEDURES

13.11.1. Calcination : Many ores carry enough moisture. Furthermore these ores are in a form which can give rise to volatile gases on heating. Calcination is a heat treatment of the ore such that the ore is not allowed to melt but is forced to get rid of moisture and unwanted volatile matter. Carbonate ores are often calcined to get rid of undesirable carbon dioxide and arsenic alongwith any moisture that it may carry.

13.11.2. Roasting : Roasting of an ore means heating of the finely ground ore in a regulated stream of air. The temperature is so maintained that the ore does not melt. Roasting is a compulsory step for sulphide and sulphide-oxide ores.

Zinc blende, ZnS, ore is first concentrated by the froth floatation process and then the concentrated ore is roasted in a controlled stream of air. The sulphide decomposes and sulphur dioxide is given off. In case too much oxygen is allowed during roasting ZnS may be converted to $ZnSO_4$, reduction of which might prove difficult.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$(ZnS + 2O_2 \rightarrow ZnSO_4)$$

The tin ore, casseterite SnO_2, is successively concentrated by running water and then by the application of a magnetic field. The enriched casseterite still contains some FeS and arsenical pyrites FeAsS. The ore is roasted under regulated supply of air when much of the sulphur and arsenic are lost in the form of SO_2 and As_2O_3 gas.

Copper pyrites, $CuFeS_2$, is first concentrated by the froth floatation procedure and is then subjected to roasting. The following reactions occur :

$$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$

Much of the accompanying arsenic and antimony are removed as their volatile oxides As_2O_3 and Sb_2O_3.

Roasting is also employed for the cobaltite ore, CoAsS, when much of the sulphur and the arsenic are removed as volatile SO_2 and As_2O_3.

13.11.3. Smelting : Many metals are recovered in molten state from their ores via chemical reactions at high temperature. Such a process is termed smelting. Recovery of iron from haematite via reactions with coke, limestone etc. in a blast furnace is a good example of smelting.

$$Fe_2O_3 + 3C \rightarrow \underset{\text{(fused)}}{2Fe} + 3CO$$

Recovery of lead from galena via reaction with coke etc. in blast furnace is also an example of the smelting process :

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2 \;;\; PbO + CO \rightarrow Pb + CO_2$$

$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2 \;;\; PbS + FeO + C \rightarrow Pb + FeS + CO$$

It is, however, always a big problem to recover the molten metal from other molten products formed during smelting. In order to achieve a separation of the molten metal from other undesirable molten species the smelting is carried out in the presence of added compounds, called *flux*, which can form chemical compounds with the impurities. These new products usually vary in their density from that of the molten metal and are known as *slag*.

In the manufacture of iron, limestone ($CaCO_3$) is added alongwith the coke. Inside the blast furnace the limestone is decomposed to CaO. This CaO then reacts with the impurity SiO_2 to form the slag calcium silicate. If the impurity is aluminium oxide the slag formed is calcium aluminate. The slag remains in the molten form above the molten iron in the bottom portion of the blast furnace (Chapter 23).

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SiO_2 \rightarrow CaSiO_3 \;;\; CaO + Al_2O_3 \rightarrow Ca(AlO_2)_2$$

A similar slag formation is made use of in the extraction of lead. After roasting of galena the roasted material is mixed with coke, limestone and little ferric oxide and reacted in a blast furnace. Molten lead settle at the bottom of the furnace while the molten slag consisting of calcium silicate and iron sulphide stay above the molten lead.

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SiO_2 \rightarrow CaSiO_3 \text{ ; } Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$

$$FeO + PbS + C \rightarrow Pb + FeS + CO$$

During the extraction of copper from copper pyrites the following reactions occur :

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \rightarrow FeSiO_3 \text{ (slag)}$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

The molten copper settles below the layer of the molten slag.

13.12. DIFFERENT EXTRACTION PROCEDURES BASED ON DIFFERENT ORES

13.12.1. Extraction of the Alkalies and the Alkaline Earths : These are the elements which have the highest negative reduction potentials. Hence the most powerful reduction technique, namely the electrolytic reduction, is employed in the extraction from their fused chlorides. For details see Table 13.1.

13.12.2. Extraction of Manganese, Chromium and Iron : The oxides of these elements may be reduced by alumino-thermite process. However iron is extracted in very large quantity and it is best done in a blast furnace.

13.12.3. Extraction of Metal from Sulphide Ores : Among the most important sulphide ores are galena, (PbS) zinc blende, (ZnS), copper pyrites ($CuFeS_2$), and cinnabar, (HgS). It is a general rule that all sulphide ores are first roasted in regulated supply of air. Much of the sulphur and any accompanying arsenic or antimony are removed as volatile oxides. The metal oxide and some of the unconverted sulphide are then mixed with coke and limestone and heated to higher temperature. The undesirable products form slag while the desired metal collects in the molten form below the layer of the slag. Details of these reactions appear in respective Chapters.

In this connection one point may be noted. The reduction of the lead sulphide and copper sulphide so occur that one might call these reactions as *self-reduction reactions* :

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2 \; : \; PbS + 2PbO \rightarrow 3Pb + SO_2$$

$$PbS + 2O_2 \rightarrow PbSO_4 \; : \; PbS + PbSO_4 \rightarrow 2Pb + 2SO_2$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \; : \; Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

EXERCISES

1. How do you correlate standard reduction potentials of metals with their extraction procedures?

2. Why carbon is preferred in most reduction procedures although hydrogen is a reducing agent of proven quality?

3. Discuss the following techniques employed in metal extractions :
(*a*) roasting (*b*) electrolysis (*c*) calcination

4. Write notes on the following :
(*a*) minerals and ores (*b*) flux (*c*) slag (*d*) electrolytic refining of metals

5. Given below are the reduction potentials of some metals. Suggest which method would be suitable in the extraction of the metals :

(*a*) Zn^{2+}/Zn ; $E^\circ = -0.76$ volts
(*b*) Ag^+/Ag ; $E^\circ = +0.79$,,
(*c*) K^+/K ; $E^\circ = -2.95$,,
(*d*) Al^{3+}/Al ; $E^\circ = -1.66$,,

6. Give some examples of precipitation of a metal ion from its complex by reaction with another metal. Explain your answer in general terms without trying to quote the standard reduction potentials.

7. Give a general account of the methods usually employed for concentration of ores.

CHAPTER 14

HYDROGEN

14.1. INTRODUCTORY COMMENTS

Hydrogen is the lightest element in the periodic table. Its atomic number is 1. It has therefore one electron in its outer orbital. The very first quantum shell ($n = 1$) can have a maximum of two electrons. The only electron, that hydrogen has, is located in the spherical $1s$ orbital. The element shows a very rich array of physical and chemical properties. These are grouped together below :

1. Its lone valence electron may be lost to generate the positively charged ion, H^+, which in reality is a proton. It is the smallest possible cation (the radius being of the order of 10^{-12} cm) and according to Fajans' rules is likely to have great deforming power. In reality we find that in aqueous medium the H^+ ion takes up one molecule of water and stays in the form H_3O^+ (Chapter 8).

2. Since the maximum capacity of the first shell is 2 electrons, the element may draw one more electron from very highly electropositive elements and thus move over to the hydride ion, H^-. This ion is isoelectronic with helium.

3. Besides the two ionic forms of its chemistry it is also known to form well defined covalent compounds with elements of similar electronegativity values. Good examples are provided by CH_4, C_2H_6 etc.

4. It forms polar covalent compounds with elements with higher electronegativity values. Polarity developed in these molecules leads to association, which in turn leads to abnormal melting points and boiling points. Examples are HF, H_2O, NH_3.

5. It also gives rise to very special three-centred-two-electron bonds in electron deficient hydride compounds like B_2H_6, B_4H_{10} etc.

6. In its diatomic molecular form the two electrons have opposite spins according to the Pauli exclusion principle. While the electrons are having opposite spins the two protons may spin (*a*) in the same direction to give *ortho-hydrogen* or (*b*) in the opposite direction to produce *para-hydrogen*.

7. The nucleus may have 0, 1 or 2 neutrons. Thus the element is known to have as many as three isotopes : protium, deuterium and tritium respectively.

14.2. ISOTOPES OF HYDROGEN

We have given several definitions of isotopes in Chapter 1. In essence isotopes have the same atomic number i.e. the same number of protons and electrons but varying number of neutrons inside the nucleus. Thus isotopes of an element vary in their mass. Of the three isotopes of hydrogen, namely ^1_1H (protium), ^2_1H (deuterium) and ^3_1H (tritium), protium is the form we usually call hydrogen. We discuss below some properties of the other two isotopes.

14.2.1. Deuterium : This isotope of hydrogen has an atomic number 1 but mass number 2. Its nucleus is composed of one proton and one neutron and hence it is twice as heavy as the ordinary (protium form) hydrogen. Because of its heaviness this isotope is also often referred to as heavy hydrogen. Ordinary hydrogen carries about 0.015% of the heavy form ${}^2_1H$. We have already seen in Chapter 2 that electrolysis is ideally suited to recovery of this isotope from ordinary water. Repeated electrolysis of alkaline water leads to concentration of heavy water (${}^2_1H_2O$ or D_2O) in the electrolytic cells. After removal of the excess alkali, distillation of heavy water gives heavy hydrogen i.e. deuterium at the cathode. Table 14.1 records some of the properties of ordinary water and heavy water.

Table 14.1. Properties of H_2O and D_2O

Property	H_2O	D_2O
1. Melting Point (°C)	0	3.82
2. Boiling Point (°C)	100	101.40
3. Specific gravity (20°C)	0.9982	1.106
4. Temperature of maximum density	4.08	11.2
5. Viscosity (millipoise)	10.09	12.6
6. Ionic mobility (H/D in H_2O/D_2O) $\times 10^5$ (cm/sec/volt at 18°C)	315.2	213.7
7. Solubility of NaCl (in gm/gm solvent) (at 25°C)	0.359	0.305

Reactions of deuterium : Since isotopes vary in their mass content but not in the number and arrangement of the extranuclear electrons we cannot expect them to show any reasonable variation in their chemical properties. Some slight variations are expected in their mass-dependent physical properties. Chemical reactions occur as a result of collision of the interacting atoms or molecules. Since deuterium or deuterium oxide is heavier than the corresponding lighter hydrogen or ordinary water it is reasonable to expect that the reactions with the heavier species will be comparatively slow. However the products and the types of reactions will be the same in both the cases. Some examples are cited below :

$$2D_2 + O_2 \rightarrow 2D_2O \quad ; \quad D_2 + Cl_2 \rightarrow 2DCl$$

$$D_2O + SO_3 \rightarrow D_2SO_4 \quad ; \quad D_2O + N_2O_5 \rightarrow 2DNO_3$$

$$C_6H_6 + 3D_2 \rightarrow C_6D_6 + 3H_2 \text{ (in the presence of platinised platinum)}$$

The hydrate water of a hydrated salt can be substituted by D_2O on repeated crystallisations from heavy water. Thus if we crystallise $NiSO_4.7H_2O$ repeatedly from heavy water we will get crystals of $NiSO_4.7D_2O$.

Uses of Deuterium and Deuterium oxide : Major current use of D_2O is in atomic reactors meant for power generation. The neutrons evolved in such reactors are either slowed down considerably or absorbed to a desired extent with the help of the heavy water. The second important use is in research. If we wish to be sure about the presence of hydrogen in a particular part of an organic molecule then the compound is repeatedly treated with D_2O when an isotopic substitution takes place. Some typical bond vibrations are shifted to lower energies. Thus if we replace the hydrogens in $-NH_2$ group by deuterium to produce $-ND_2$ then in the infra-red spectra of the compound the original N—H absorption bands will be missing and will be replaced by newer bands at lower energy.

Tritium : This is the heaviest isotope of hydrogen of atomic number 1 but mass number 3. It is present in nature in practically negligible quantity. It is obtained by artificial transmutation reactions : (*a*) by bombardment of lithium-6 by neutron or (*b*) by bombardment of beryllium-9 by deuteron :

$$(a)\quad {}^{6}_{3}\mathrm{Li} + {}^{1}_{0}n \rightarrow {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{H}\ (= {}^{3}_{1}\mathrm{T})$$

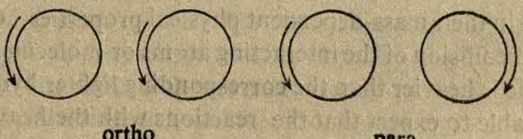
$$(b)\quad {}^{9}_{4}\mathrm{Be} + {}^{2}_{1}\mathrm{D} \rightarrow 2\,{}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{H}$$

Tritium is radioactive and is a beta-emitter :

$${}^{3}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + {}^{0}_{-1}e$$

14.3. ORTHO-HYDROGEN AND PARA-HYDROGEN

These two forms of hydrogen molecule are regarded as nuclear isomers. In para-hydrogen the two protons of the two hydrogen atoms spin in opposite direction about their axes while in the ortho-hydrogen the spins of the two protons are in the same direction (Fig 14.1). It is evident that the total energy content of para-hydrogen is less than the ortho-isomer. The para-form is symmetrical while the orthoform is not. On increasing temperature the para form goes over to the ortho form. Around absolute zero hydrogen remains almost entirely in the para form. At ordinary temperature molecular hydrogen consists of 25% para and 75% ortho forms. It is to be appreciated that chemically both the ortho and the para forms are similar. Thermal conductivity of the para form is higher than the ortho form.



ortho para

Fig. 14.1. Ortho and para forms of molecular hydrogen

These two forms of hydrogen should not be confused as examples of allotropes. It is true that like allotropes these are two forms of the same element in the same physical state. But unlike allotropes there is no difference in their molecularity or in the nature of their chemical bonding (Chapter 10).

14.4. NASCENT HYDROGEN

This is a form of hydrogen which is more active than the ordinary molecular hydrogen. This active form is generated during synthesis of molecular hydrogen. It is believed to be the atomic form of hydrogen prior to its going over to the diatomic covalent molecular H_2. The usual methods of obtaining nascent hydrogen are : (*a*) reaction between a metal and an acid (*b*) reduction by sodium amalgam in aqueous medium and (*c*) during electrolysis of water with cathodes which are known to release hydrogen rather late. The reactivity of nascent hydrogen as a reductant is dependent on the particular method of synthesis. This is because of the fact that the energy of the nascent hydrogen varies according to the procedure adopted in its synthesis.

Nascent hydrogen is a far superior reducing agent than the ordinary molecular hydrogen. Some reduction reactions which cannot be accomplished by ordinary form of the hydrogen can be achieved by nascent hydrogen :

$$KClO_3 + 6H \rightarrow KCl + 3H_2O \ ; \ FeCl_3 + H \rightarrow FeCl_2 + HCl$$

If we bubble hydrogen gas through acidified $KMnO_4$ or $K_2Cr_2O_7$ there is no reduction. But reduction of these compounds does occur when these solutions are treated with zinc and H_2SO_4 :

$$2KMnO_4 + 3H_2SO_4 + 1OH \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 6H \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

14.5. ATOMIC HYDROGEN

Molecular hydrogen can be atomised by the application of heat. This atomisation reaction is endothermic and needs about 103 KCal of heat : $H_2 + 103\ KCal \rightarrow H + H$. It follows that the reverse reaction i.e. formation of molecular hydrogen from atomic hydrogen will be exothermic i.e. will liberate the same amount of energy as has been necessary during atomisation. Langmuir first utilised this liberated energy in fusing metal plates in a completely reducing atmosphere.

Atomisation of molecular hydrogen is possible by passing gaseous molecular hydrogen at low pressure (0.01 mm) over tungsten, platinum or palladium metals heated to around 2000°C. Molecular hydrogen can also be atomised by passing the gas at low pressure through an electric discharge maintained between two tungsten electrodes. Langmuir's device for atomising hydrogen and utilising atomic hydrogen for metal welding is called atomic hydrogen blowpipe. This provides a temperature as high as around 4000°C. Oxygen-acetylene and oxygen-hydrogen torches give temperatures upto around 3200°C and 2800°C respectively.

Atomic hydrogen is a more powerful reducing agent than ordinary hydrogen. Atomic hydrogen can reduce permanganate [manganese (VII)] to manganous state [manganese (II)], potassium dichromate [chromium (VI)] to chromic state [chromium (III)], mercuric salts to mercury, cupric salts to copper metal, silver nitrate to metallic silver etc.

14.6. ELECTROCHEMICAL SERIES

Electrochemical series is an arrangement of the elements according to their chemical reactivity. This series was developed even before our knowledge on the reduction potentials of metals had crystallised. It is now seen that there is a good correlation among the positions of the metals in the electrochemical series and their reduction potentials. The following salient points may be noted :

I. The elements at the top of the series are very reactive indeed. They liberate hydrogen from water and acids. The solution ultimately turns alkaline. We now know that these are the elements with high negative reduction potentials (Chapter 7). Alkalies and the alkaline earths belong to this group.

II. The next group of elements are less reactive compared to the first group. They too react with water but rather slowly. The reaction goes better with hot water or when steam is allowed to react with the heated metals. Examples of this class are magnesium, aluminium, manganese, zinc, chromium, iron etc.

III. The next class of elements comprising cobalt, nickel, tin, lead etc react even slowly with steam. However they do react well with strong acids to liberate hydrogen and to form corresponding salts. The reduction potentials of these elements are negative but not as negative as those of the alkalies or the alkaline earths.

IV. The next class of elements are below hydrogen. They cannot liberate hydrogen from acids. They however react with acids which are oxidising in nature. Depending on the nature of the oxidising acid gases like NO_2 (from HNO_3) or SO_2 (from H_2SO_4) are given off. A scrutiny shows that these elements have positive reduction potentials. This means that these elements release their electrons less readily than hydrogen. As a result they cannot supply electrons to the hydrogen ions of acids to make neutral hydrogen. Thus no liberation of hydrogen takes place.

V. The last two elements at the very bottom of the series are gold and platinum. These two react slowly even with aqua regia.

Table 14.2. Electrochemical Series

I. Reduction potentials are negative ; react vigorously with water; and acids	Li K Ba Sr Ca Na	Their oxides cannot be reduced by hydrogen or carbon monoxide ; Electrolysis of fused salts or reduction by more reducing elements is necessary for their extraction
	Mg	
II. Reduction potentials are less negative than those of I ; less reactive ; reacts with steam or acids.	Al	
	Mn Zn Cr Cd Fe	Their oxides may be reduced by aluminium or carbon at elevated temperature ;

Table 14.2. Electrochemical Series (continued)

III. Reduction potentials are negative but quite poor ; reacts with acids but not with water	Co Ni Sn Pb H	Their oxides may be reduced by hydrogen or carbon monoxide at high temperature
IV. Reduction potentials are positive ; reacts with oxidising acids ; reacts with oxidising acids ; reacts with other acids in presence of air.	Cu As Bi Sb Hg Ag	
V. Reduction potentials are very positive ; inactive ; reacts with aqua regia	Au Pt	These oxides are decomposed by heat alone.

14.7. BINARY HYDRIDES

Compounds containing hydrogen and a second element are in general termed binary hydrides. Although in a strict sense the word 'hydride' means a compound where hydrogen is present as an anion, the term is used in a larger sense to cover all binary compounds containing hydrogen and one other element. Depending on the nature and properties binary hydrides have been broadly classified into three groups : (*a*) ionic hydrides (*b*) covalent hydrides and (*c*) transition metal or interstitial hydrides.

14.7.1. Ionic Hydrides : These are the hydrides formed by the combination of the strongly electropositive alkali and the alkaline earths. Elements located at the left-hand corner of the long-form of the periodic table form these hydrides (Table 14.3). These elements are known to have very low ionisation potential and quite negative reduction potentials. Thus they easily transfer their valence electrons to hydrogen making the latter a negative hydride ion. These hydrides therefore behave as salts. Typical of salts in fused state these hydrides conduct electric current. Electrolysis of the fused ionic hydrides gives the metal at the cathode while hydrogen is liberated at the anode.

$$LiH \rightarrow Li^+ + H^-$$

at the cathode : $Li^+ + e \rightarrow Li$

at the anode : $H^- \rightarrow H + e \; ; \; 2H \rightarrow H_2$

In the formation of the ionic hydrides the role of hydrogen is that of an oxidant as it receives the electron released from the alkali or the alkaline earth metals. Usually hydrogen reacts with these elements in the temperature range 300-600°C. The crystal structure of these hydrides resemble those of comparable ionic compounds.

Table 13.3. Classification of Binary Hydrides based on Long form Periodic Table

	IA	IIA											IIIB	IVB	VB	VIB	VIIB	0
Period I	H																	He
Period II	Li	Be											B	C	N	O	F	Ne
Period III	Na	Mg	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	Al	Si	P	S	Cl	Ar
Period IV	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Period V	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Period VI	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Ionic Hydrides			Transition metal Hydrides											Covalent Hydrides				

14.7.2. Covalent Hydrides : These hydrides are formed as a result of covalent bonding between hydrogen and the second element. It can be guessed that in order for a covalent bond to be operative the electronegativities of hydrogen and the other reacting elements must not vary too much. If the electronegativities are very close the resulting compounds will be non-polar hydrides eg. CH_4, C_2H_6 etc. If there is a substantial difference then we will get polar hydrides eg. NH_3, HF, H_2O. We have already seen in Chapter 5 that such binary hydrides are associated and give rise to abnormal melting and boiling points.

Typical of covalent compounds these hydrides are nonelectrolytes. In a group of comparable non-polar covalent hydrides the melting points and boiling points increase with increasing molecular weights. But the associated hydrides NH_3, H_2O and HF are exceptions in the respective groups. Their general methods of syntheses are : (*a*) direct union of the elements in the presence or absence of catalysts and (*b*) decomposition of another suitable binary compound of the hydride forming element by acids or water :

$$N_2 + 3H_2 \xrightarrow[400^\circ C/200\ \text{atm.}]{\text{catalyst}} 2NH_3$$

$$Mg_2Si + 4HCl \longrightarrow SiH_4 + 2MgCl_2$$

$$Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$$

14.7.3. Transition Metal Hydrides : The wide middle region elements of the long-form periodic table form these hydrides. It is however open to criticism whether we can call these compounds true hydrides. Most of these elements do not give any hydride of any definite composition. In most cases the hydrogen in-take depends on the reaction conditions. Hydrogen is mostly adsorbed or occluded. The hydrogen penetrates into the interstices of the metallic structure of the transition metals resulting in an expansion of the metal lattice. In general finely divided transition metals at certain optimum temperature take up hydrogen to form such hydrides eg. $TiH_{1\cdot78}$, $ZrH_{1\cdot9}$; $VH_{0\cdot6}$ etc. Palladium has the highest capacity to occlude hydrogen. This property has been made use of in obtaining very pure form of hydrogen.

14.8. POSITION OF HYDROGEN IN THE PERIODIC TABLE

In Chapter 3 we have seen that hydrogen can be placed either at the head of the group IA or at the head of group VIIB. Some texts point this out as a defect of the periodic table. But this cannot be entertained seriously as it only highlights the fact that we are dealing with an element of dynamic personality. In the acid form H^+ it is monopositive like the alkalies. In fact when acidified water is electrolysed hydrogen is liberated at the cathode. Compare the fact that electrolysis of fused alkali halides gives the corresponding alkali metals at the cathode. So position of hydrogen in group IA above the alkalies is entirely justified.

electrolysis of fused NaCl : at the cathode : $Na^+ + e \rightarrow Na$

electrolysis of acid water : at the cathode : $2H^+ + 2e \rightarrow H_2$

Also to be noted is the comparable electron arrangement. All the alkalies have their single valence electron in the outermost *s* orbital and so also our hydrogen : Na : $1s^2\ 2s^2\ 2p^6\ 3s^1$; H : $1s^1$. So by virtue of its having a single electron in the very first orbital it has every right to be placed in the first group of the periodic table.

Now let us see what justifications are there for the inclusion of the element in group VIIB. The halogens are just one electron short of the stable electronic configuration of the next noble gas. Similarly hydrogen is also one electron short of the next noble gas helium. Compare the following electronic configurations :

$$\text{H} : 1s^1 \quad ; \quad \text{He} : 1s^2$$
$$\text{F} : 1s^2\ 2s^2\ 2p^5 ; \quad \text{Ne} : 1s^2\ 2s^2\ 2p^6$$

On electrolysis of the fused halides halogens are liberated at the anode. Similarly on electrolysis of fused hydrides hydrogen is liberated also at the anode :

electrolysis of fused NaCl : *at the anode* : $2Cl^- \rightarrow Cl_2 + 2e$
electrolysis of fused NaH : *at the anode* : $2H^- \rightarrow H_2 + 2e$

14.9. INDUSTRIAL PREPARATION

14.9.1. Lane Process : The basic reaction is that between steam and heated iron powder. Ferroso-ferric oxide and hydrogen are formed :

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

The ferroso-ferric oxide is recovered by reacting with water gas ($CO + H_2$)

$$Fe_3O_4 + 4CO \rightleftharpoons 3Fe + 4CO_2$$
$$Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O$$

The mixture of H_2 and CO_2 is passed under pressure through water when CO_2 dissolves but hydrogen passes on. In this process hydrogen is made not at the cost of iron but at the cost of cheap coke used in the preparation of the water gas.

14.9.2. Bosch Process : In this process water gas is produced by the reaction of heated steam and heated coke. This reaction is endothermic :

$$C + H_2O \xrightarrow{1000°C} H_2 + CO\ (-29\ \text{KCal})$$

In order to keep up the supply of the heat another exothermic reaction between heated coke and air resulting in the formation of CO_2 and heat is made to go on. The exothermic and the endothermic reactions are carried out in turn. The water gas is then mixed up with excess steam and passed over a catalyst bed of Fe_2O_3 and Cr_2O_3 at 500°C. The final reaction gives a mixture of hydrogen and carbon dioxide as in the above Lane process. The mixture is then led under 25 atm. pressure through water when the carbon dioxide dissolves out while hydrogen comes out.

$$(H_2 + CO) + H_2O \xrightarrow[\sim 500°C]{Fe_2O_3 + Cr_2O_3} 2H_2 + CO_2$$

If there is any carbon monoxide coming alongwith the hydrogen it is absorbed by ammoniacal cuprous chloride in the form CuCl.CO. Thereafter pure hydrogen is obtained.

14.9.3. Electrolysis of Alkaline Water : It is a well known fact that H_2O is a poor conductor. However acidulated water or alkaline water is a conductor and evolves hydrogen at the cathode and oxygen at the anode. In the industrial scale Knowles method is taken advantage of. The electrolytic cell is an iron tank into which are suspended alternately iron plates and nickel-plated iron plates. The iron plates serve as the cathode while the nickel-plated iron plates act as anodes. In order to prevent any mixing of the hydrogen evolved at the cathode and the oxygen at the anode the plates are separated by porous asbestos sheet. The electrolyte is water made alkaline with NaOH or $Ba(OH)_2$.

14.10. PURE HYDROGEN

Very pure hydrogen may be obtained by passing hydrogen obtained by the usual methods successively through aqueous KOH and red-hot copper powder. The gas is thus rid of any moisture and oxygen. Any oxygen is trapped by the red-hot copper as cupric oxide. Finally the gas is adsorbed by powdered palladium. On heating this palladium hydride very pure hydrogen is given off.

14.11. USES OF HYDROGEN

This element finds varied uses in industry and research spheres. Some of its important uses are enumerated below :

1. A host of compounds of industrial importance are made via hydrogen :

$$N_2 + 3H_2 \rightarrow 2NH_3 \quad ; \quad 2H_2 + CO \rightarrow CH_3OH$$

2. It is profusely used in hydrogenation of oils like coconut oil, cotton seed oil etc. to produce products like dalda, margarine etc. The reactions are essentially addition of hydrogen to double bonds of the unsaturated hydrocarbons present in these oils. The reactions are usually carried out in the presence of powdered nickel as hydrogenation catalyst.

3. It is also used in atomic hydrogen blow-pipe for welding purposes. It has an added advantage over other such welding torches in that it creates a perfectly reducing atmosphere around the metal pieces to be welded.

4. Heavy water finds use in atomic reactors. The evolved neutrons are either slowed down or considerably absorbed so as to regulate the liberation of energy.

14.12. SOFT WATER AND HARD WATER

During the rainy season the rain water percolates, through large number of layers, deep into the soil. While passing through these layers the water dissolves out soluble bicarbonates, chlorides and sulphates of mostly calcium and magnesium.

Sometimes some iron compounds are also found in the water that is pumped out from below the surface soil. Surface water of rivers, tanks etc. also absorb lot of atmospheric carbon dioxide to form bicarbonates.

The quality of the water at our disposal decides the solubility of chemicals. One practical index of deciding about the quality of water is by way of its producinglather with soap. The major constituent of soap is sodium stearate $NaC_{18}H_{35}O_2$. The calcium and magnesium salts of this organic acid are insoluble in water. Thus if a water specimen contains substantial amount of soluble calcium and magnesium salts it will not produce lather with soap as long as these salts are present in water :

$$Mg^{2+}/Ca^{2+} + 2C_{18}H_{35}O_2^- \rightarrow (Mg^{2+}/Ca^{2+})(C_{18}H_{35}O_2^-)_2 \downarrow$$

The insoluble stearates will continue to be precipitated as long as the soluble calcium and magnesium salts are present. *That water is called soft water which easily produces lather with soap.* On the contrary *that water is termed hard water which does not readily form lather with soap.*

Depending on the type of soluble salts present in water hard water has been classified in two groups : (*a*) temporary hard water contains soluble bicarbonates of calcium (II) and magnesium (II) and (*b*) permanent hard water contains chlorides or sulphates of calcium (II) and magnesium (II). Hard water is a menace both for house-hold purposes and in the industries. In industries hard water spoils the boilers because of deposits of insoluble carbonates and sulphates of calcium and magnesium. Presence of other metal salts may also complicate matters.

14.12.1. Removal of Temporary Hardness : Since temporary hardness is due to the presence of soluble bicarbonates it can be easily removed by mere boiling when the bicarbonates are converted to the insoluble carbonates. The water obtained on filtration is soft.

$$Ca(HCO_3)_2 \xrightarrow{\text{heat}} CaCO_3 + CO_2 + H_2O$$

$$Mg(HCO_3)_2 \xrightarrow{\text{heat}} MgCO_3 + CO_2 + H_2O$$

The white crust that we always observe in our tea-kettles is due to insoluble $CaCO_3$ and $MgCO_3$. This can be dissolved out by treating the mass with a weak acid like vinegar.

14.12.2. Removal of Permanent and Temporary Hardness : Several methods are in use.

I. LIME SODA PROCESS : This is the oldest method. In order that this method becomes effective the hard water has to be carefully analysed for its calcium, magnesium and bicarbonate contents. Based on these analyses the hard water is treated with calculated amounts of sodium carbonate and lime i.e. calcium hydroxide. The sodium carbonate removes calcium and magnesium as the insoluble $CaCO_3$ and $MgCO_3$ while the lime is intended to remove the bicarbonate ion. The following reactions take place :

$$(a)\ CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$$

$$(b)\qquad Ca(OH_2) \rightarrow Ca^{2+} \quad + 2OH^-$$

$$(c)\qquad Ca(HCO_3)_2 \rightarrow Ca^{2+} \quad + 2HCO_3^-$$

$$2HCO_3^- + 2OH^- + Ca^{2+} \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

Essentially the OH^- ions of lime react with the HCO^-_3 ions to form CO_3^{2-} ion and H_2O. Then the Ca^{2+} of lime forms the insoluble $CaCO_3$. Excess of lime has to be avoided as it will again make the water hard. This is the major shortcoming of this method.

II. CALGON PROCESS : Sodium metaphosphate, $NaPO_3$, is in reality sodium hexametaphosphate $Na_2[Na_4(PO_3)_6]$. This reagent can react with calcium and magnesium salts to form insoluble complex salts :

$$Na_2[Na_4(PO_3)_6] + CaCl_2 \rightarrow 2NaCl + Na_2[Na_2Ca(PO_3)_6]$$

The reagent sodium metaphosphate is made by heating sodium ammonium hydrogen phosphate :

$$NaNH_4HPO_4 \rightarrow NaPO_3 + NH_3 + H_2O$$

The term 'calgon' means 'calcium gone'. Calgon cannot be used over and over again.

III. ZEOLITE PROCESS : Natural zeolites are complex silicates of the types : $NaAlSiO_4$; $NaAlSi_2O_6$; $NaAlSi_3O_8$. These complex silicate ions have large holes or cavities within them. These holes are usually occupied by the sodium ions. The silicate ions are much too big to participate in any exchange reactions. These silicates are normally insoluble in water and can exchange their sodium ions for calcium ions or similar ions. Thus the calcium and magnesium ions normally present in hard water, when allowed to pass through a bed of these zeolites, undergo exchange reactions. The calcium and magnesium ions are retained on the zeolite bed and the effluent liquid is soft water containing sodium ions :

$$Ca^{2+} + 2NaZ \rightleftharpoons CaZ_2 + 2Na^+ ;\ Mg^{2+} + 2NaZ \rightleftharpoons MgZ_2 + 2Na^+$$

$$(Z^- \rightleftharpoons \text{zeolite anion})$$

It can be inferred that the softening power of such zeolites are limited by their exchange capacity. It follows that after a number of such exchanges all the exchangeable sodium ions of the zeolite will be exhausted and the zeolite will be ineffective. When this stage is reached the exhausted zeolite is treated with a very large excess of sodium ions. Under the mass action of sodium ions the calcium ions are now replaced by the sodium ions. Thus the zeolite is said to be regenerated. It is then ready for further use as a softening material.

Zeolites can now be prepared synthetically. A gel of silica and alumina is carefully treated under strict reaction conditions with sodium chloride when the syntheitc zeolite crystallises. Synthetic zeolites have the general formula : $Na_2O.Al_2O_3.nSiO_2.mH_2O$. Synthetic zeolites are called 'permutits'. The exchange reactions can be expressed as :

$$Na_2\text{-permutit} + CaCl_2 \rightleftharpoons 2NaCl + Ca\text{-permutit}$$

One interesting thing should be noted. In none of the above three methods do we have the water free from any ions. In all the cases we have the calcium and the magnesium ions replaced by the sodium ion. It is true that hard water is rendered soft but the water is not de-ionised. We now describe the most powerful synthetic method which can give us the ideal de-ionised water.

IV. ION-EXCHANGE RESINS : These are synthetic resinous materials which can exchange cations or anions depending on the compositions of the resin. These resins have a polymeric cationic or anionic unit alongwith a small anion or cation to maintain electroneutrality. *Those resins which can exchange cations are called cation exchange resins while those which can exchange anions are known as anion exchange resins.*

Cation Exchange Resin : A common cation exchange resin is made out of polymerisation of styrene ($C_6H_5 - CH = CH_2$) and divinyl benzene ($CH_2 = CH-C_6H_4 - CH = CH_2$). The polymer is then sulphonated by usual procedure (Fig. 14.2). A look at this resin shows that the only ion which has some freedom of movement is the hydrogen ion (H^+). The rest is the polymeric anion which serves as the backbone of the resin. The small hydrogen ions are the exchangeable ions of the resin. The resin, being polymeric, is insoluble in water and its polymeric anion is nonexchangeable. If such a resin is treated with sodium ions its hydrogen ions will be replaced by sodium ions and the effluent will carry the released hydrogen ions. After the hydrogen ions are substantially exchanged by other cations the resin can be revitalised by treatment with sufficient dilute acid When the replaceable ions of the resin are hydrogen ions the resin is said to be

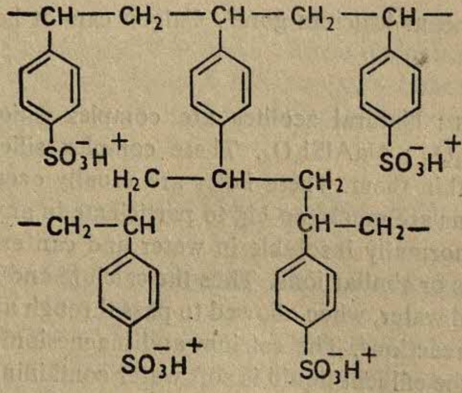


Fig 14.2. A cation exchange resin

in the hydrogen form. If the replaceable ions are sodium ions the resin is said to be in the sodium form and so on.

Anion Exchange Resin : An anion exchange resin has to have a polymeric cation as the insoluble backbone, incapable of any exchange reaction, and a small anion which can participate in exchange reactions.

A typical anion exchange resin (Fig. 14.3) is made of polymerisation of styrene and divinyl benzene, being followed by chloromethylation reaction. This last reaction introduces $-CH_2Cl$ radical at suitable points of the polymeric resin.

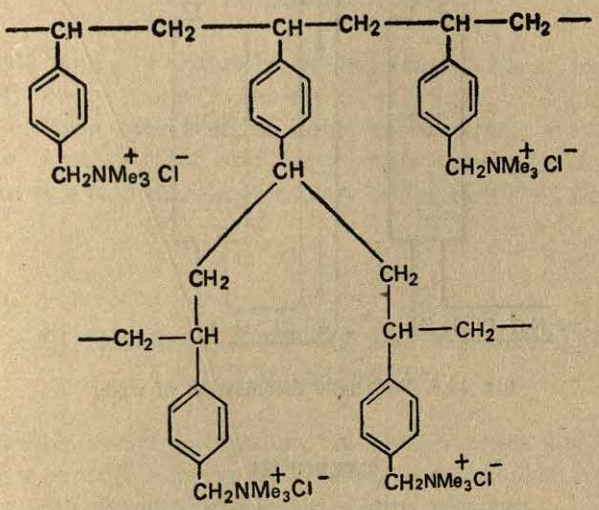


Fig. 14.3. An anion exchange resin

The resin is then reacted with a base like trimethylamine,. It can be seen that the only part that has any freedom of movement is the small chloride anion. If a column packed with such a resin is treated with sufficient NaOH all the chloride anions of the resin bed will be replaced by OH^- ions. The resin will then go over to the hydroxide form.

Preparation of Deionised Water : We can achieve the preparation of deionised (i.e. ion-free) water with the help of a hydrogen form cation exchange resin and a hydroxide form anion exchange resin. This is accomplished in a set-up shown in Fig. 14.4. The hard water is first led through a hydrogen form cation exchanger (HZ). The cations are retained on the resin bed while the exchanged H^+ ion alongwith the unchanged anions are then forced into a column packed with hydroxide form anion exchanger (ROH). The anions present in the water are now retained on the resin bed while the exchanged OH^- ions are released. The solution passing out of the column now contains equal number of H^+ and OH^- ions i.e. we get pure deionised water. It is now-a-days a common practice to have deionised water in chemical laboratories rather than age-old distilled water. However the reader should appreciate that the distilled water, usually obtained by distillation of water in electric stills or copper heaters, gives not only ion-free water but also germ-free water. But deionised water obtained through two types of ion exchangers is free from ions but not free from germs. Deionised water is also not free from any covalent impurity present originally in the water. Distilled water is also likely to be free from such covalent impurities.

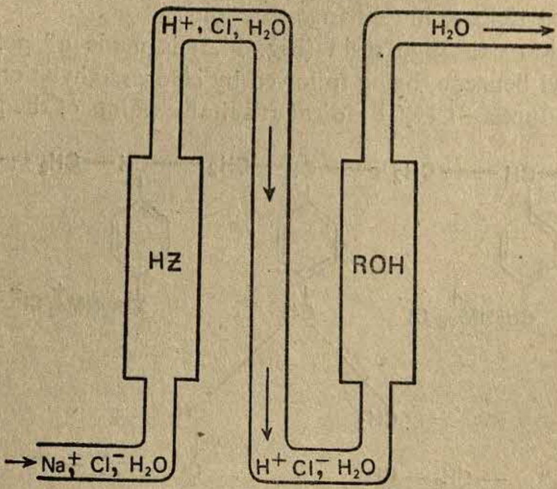


Fig. 14.4. Schematic deionisation of water

EXERCISES

1. Give a concise resume of the modes of reactivity of hydrogen in its elementary state as well as in compound states.

2. Discuss the position of hydrogen in the periodic table.

3. What are isotopes? Name and give the characteristic properties of the different isotopes of hydrogen.

4. How would you proceed to prepare heavy water? What is its modern use?

5. Would you consider ortho- and para-hydrogen as allotropic modifications? Present a short account of these two forms of hydrogen.

6. Give a classification of binary hydrides. Indicate in the log form periodic table the positions of the different elements forming the different types of hydrides. How does the nature of bonding vary in these compounds?

7. How is lithium hydride obtained? How is it known that hydrogen is present in this compound in the form of an anion? Do you think hydrogen acts as an oxidant during the synthesis of lithium hydride?

8. Give a concise account of industrial preparations and uses of hydrogen.

9. Write an essay on the different methods available for removal of hardness of water.

10. Is there any distinction between soft water and deionised water? Are deionised water and distilled water the same?

CHAPTER 15

GROUP IA : THE ALKALI METALS

15.1. INTRODUCTION

The alkali metals belong to Group IA of the periodic table. They form one of the most closely related groups in the entire periodic table. All of them have a single valence electron over a stable noble gas electronic configuration. This valence electron s easily lost and their entire chemistry is dominated by their ions. Thus it is said that the chemistry of the alkalies is the chemistry of their ions.

15.2. A COMPARATIVE STUDY OF THE CHEMISTRY OF THE ALKALIES

The elements lithium, sodium, potassium, rubidium, caesium and the radioactive francium together constitute this group. Leaving aside francium we will now look into the physical and chemical properties of these elements.

Physical Properties : 1. Their electron distribution (Table 15.1) shows that all of them have a single valence electron above a stable noble gas core. This electron distribution has identified them as members of the group IA of the periodic table.

2. Their first ionisation potentials are in general low compared to other elements and these potentials continue to decrease, as expected, with increasing atomic numbers. This tells us that ionic i.e. metallic character increases with increasing atomic number.

3. Their electronegativities are quite low (cf. fluorine, 4.0) and that too decrease, according to rules, from lithium to caesium. This points to the fact that these elements have very little tendency to have a share of electrons in covalent bonds.

4. As expected wth increasing atomic number the ionic radii also increase from lithium to caseium.

5. Their reduction potentials are the most negative. This indicates that they readily tend to give up their valence electron and thus go over to the monopositive cations. Their chemistry is thus dominated by the chemistry of their ions. It also follows that it is really difficult to reduce their ions back to the metallic forms.

6. With increasing atomic number the elements become soft. This is indicated by their decreasing melting points.

Table 15.1. A Comparison of some Properties of the Alkalies

Element	Atomic Number	Electron Distribution	Ionisation Potential (*ev*)	Electronegativity	Ionic Radius (A)	Reduction Potential $M^+ + e \rightleftharpoons M$(volts)	M.P. (°C)
Li	3	$[He]2s^1$	5.39	1.0	0.60	−3.04	174
Na	11	$[Ne]3s^1$	5.14	0.9	0.95	−2.71	97.9
K	19	$[Ar]4s^1$	4.34	0.8	1.33	−2.92	63.7
Rb	37	$[Kr]5s^1$	4.18	0.8	1.48	−2.99	38.5
Cs	55	$[Xe]6s^1$	3.89	0.7	1.69	−3.02	28.5

Chemical Properties : 1. All these elements react with water forming hydroxide and liberating hydrogen : $2M + 2H_2O \rightarrow 2MOH + H_2$. The reaction becomes more violent with increasing atomic number.

2. The reactivity towards oxygen also continues to increase with increasing atomic number. Lithium gives monoxide and sodium upto peroxide while the heavier metals give upto superoxide MO_2.

3. The reaction with halogens is also violent and the reactivity increases with increasing atomic number. The resulting halides are all perfectly ionic as is revealed by their ionic crystal structure and conductivity in the fused state.

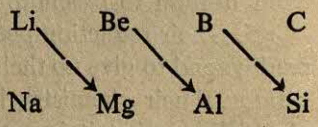
4. The electron releasing tendency is so very great that they pass on the valence electron to hydrogen forcing the latter to move over to the negative hydride anion. We have already seen in Chapter 14 that such hydride can be electrolysed in the fused state when hydrogen is evolved at the anode instead of at the cathode :

$$LiH \rightarrow Li^+ + H^- \text{ ; \textit{at the anode} : } 2H^- \rightarrow H_2 + 2e$$

5. The highly cationic properties of these ions, particularly the heavier ones, make them ideally suitable to give solid crystals of the very weak anions like bicarbonates, bisulphites and polyhalides (HCO_3^-, HSO_4^-, I_3^-).

15.3. LITHIUM

15.3.1. Diagonal Relationship with Magnesium : Although lithium is the first member of the alkalies yet it has some similarities with magnesium, the diagonal member of group IIA. There are two other similar diagonal pairs in the periodic table : Be, Al ; B, Si. Let us first investigate what makes these two elements belonging to two neighbouring groups show comparable properties. As we move along a group charge on the cation remains the same but the size increases. Thus cationic properties tend to increase. On the other hand when we move from one group to the next in the same period charge increases and size decreases. This leads to a decrease in ionic properties and increase in covalent character. Thus



following Fajans a diagonal movement from lithium to magnesium either via beryllium or via sodium is likely to produce elements of comparable deforming ability. Elements related diagonally have rather comparable charge/ionic radius ratio :

	Lithium	Magnesium
Charge on the ion	+1	+2
Ionic radius (A)	0.60	0.65
Charge/Ionic radius	1.60	3.08

In later periods this diagonal relationship is not much prominent because of the fact that the size and charge of the ions vary but little and hence the deforming powers of the ions are not very prominent.

Similarities of properties of lithium and magnesium : Both the elements form nitrides (Li_3N and Mg_3N_2) and are used in the removal of nitrogen. Both the elements give sparingly soluble hydroxides and their carbonates are easily decomposed by heat :$Li_2CO_3 \rightarrow Li_2O + CO_2$; $MgCO_3 \rightarrow MgO + CO_2$. Lithium and magnesium fluorides are sparingly soluble in water while their perchlorates are highly soluble. Note that the points where lithium resembles magnesium are the points where lithium differs from the rest of the alkalies.

15.3.2. Differences in the Properties of Lithium and the other Alkalies : 1. Lithium reacts with nitrogen far readily compared to the other alkalies.

2. Compared to the perchlorates of the other alkalies lithium perchlorate is highly soluble in water. Note $KClO_4$ is so insoluble that this can be made use of in the gravimetric estimation of potassium.

3. Lithium ion is the smallest in the family of the alkalies. Due to unfavourable size lithium does not form any alum type double sulphate.

4. Lithium fluoride is much less soluble compared to the fluorides of the other alkalies.

5. Lithium carbonate and phosphate are insoluble while these salts of the other alkalies are quite soluble.

6. While the big sized alkalies can give superoxides (KO_2, RbO_2 and CsO_2 lithium can go upto monoxide only (Li_2O).

15.3.3. Some Compounds of Lithium : Syntheses and properties of a few selected compounds are described below :

Lithium Hydride : Lithium metal and hydrogen react around 600°C to form LiH. The compound reacts with water to form LiOH and hydrogen :

$$LiH + H_2O \rightarrow LiOH + H_2$$

On electrolysis of fused LiH hydrogen is liberated at the anode :

at the cathode : $Li^+ + e \rightarrow Li$

at the anode ; $2H^- \rightarrow H_2 + 2e$

Lithium Chloride : Its preparation involves reaction of lithium hydroxide/carbonate with HCl. The solution thus obtained is treated with HCl gas when crystals of LiCl separate out. Unlike NaCl and chlorides of the other alkalies LiCl is soluble in alcohol or pyridine. Lithium metal is extracted from its natural ores via electrolysis of this compound.

Lithium Sulphate : It can be guessed that it can be obtained as the neutralisation product of lithium hydroxide and sulphuric acid. It crystallises as the monohydrate : $LiSO_4.H_2O$.

Lithium Carbonate: Sodium carbonate reacts with soluble lithium salts to precipitate Li_2CO_3. This decomposes on heating to Li_2O and CO_2.

15.3.4. Industrial Preparation of Lithium : Both of the two important ores of lithium are silicates : lepidolite, $Li_3Al(SiO_3)_3$ which also contains Na^+, K^+ and F^- ions and spodumene $LiAl(SiO_3)_2$.

These ores are usually fused with barium carbonate and potassium sulphate. The fused mass is treated with HCl and then filtered. The filtrate contains soluble salts of lithium, barium, aluminium and potassium while silica is left behind. The filtrate is dried up and the entire mass is treated with alcohol. This treatment brings lithium chloride alone into the solution. The mixture is filtered and the lithium chloride recovered after removing the alcohol.

Anhydrous lithium chloride is fused and electrolysed. Carbon rod serves as the anode and iron rod as the cathode. The metal collected at the cathode is removed and stored under kerosene. The chlorine liberated at the anode is led away from the anode chamber and is reserved as an important by-product.

$$LiCl \rightarrow Li^+ + Cl^-$$

at the cathode : $Li^+ + e \rightarrow Li$

at the anode : $2Cl^- \rightarrow Cl_2 + 2e$

Uses : The metal finds use in the removal of nitrogen as lithium nitride : $6Li + N_2 \rightarrow 2Li_3N$.

15.4. SODIUM

15.4.1. Some Compounds of Sodium : Syntheses and properties of more important compounds of sodium are given below:

Sodium Monoxide : The usual synthetic procedure involves heating of sodium azide and sodium nitrite (or nitrate) in a nickel vessel :

$$3NaN_3 + NaNO_2 \rightarrow 2Na_2O + 5N_2$$

It is a colourless compound which reacts vigorously with water :

$$Na_2O + H_2O \rightarrow 2NaOH$$

Sodium Peroxide : Sodium metal is reacted with excess of air in aluminium vessel : $2Na + O_2 \rightarrow Na_2O_2$. It is a yellow, reactive compound. It is a good oxidant and is used in many oxidimetric reactions in the laboratory :

$$Na_2O_2 + CO \rightarrow Na_2CO_3 \; ; \; 2Na_2O_2 + 2CO_2 \rightarrow 2Na_2CO_3 + O_2$$

$$2Cr_2O_3 + 4Na_2O_2 + O_2 \rightarrow 4Na_2CrO_4$$

$$Na_2S + 4Na_2O_2 \rightarrow Na_2SO_4 + 4Na_2O$$

It is readily decomposed by water giving H_2O_2 and O_2 :

$$Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2 \; ; \; 2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

It is used (*a*) in the laboratory as an oxidant, (*b*) in decolourisation of silk and wool and (*c*) in the preparation of H_2O_2.

Sodium Hydroxide : This is one of the most important commercial compounds. It is profusely used in the manufacture of paper, soap, etc. as also in the laboratory.

In Table 15.2 a comparative assessment of the three preparative methods, namely (*a*) causticising, (*b*) Castner-Kellner and (*c*) Nelson method is given. In this connection the following points appear relevant :

Both the Castner-Kellner and Nelson methods make use of the electrolysis of saturated sodium chloride solution i.e. brine (6*M*). In the Castner-Kellner technique mercury is used as the cathode. The reduction potentials of the different systems are given for a critical inspection :

$$Na^+ + e \rightleftharpoons Na \; ; \; E^\circ = -2.71 \text{ volts}$$

$$6M \text{ NaCl} \; ; \; Na^+ + e \rightleftharpoons Na \; ; \; E^\circ \simeq -2.6 \text{ volts}$$

$$2H^+(1.0 \times 10^{-7}M) + 2e \rightleftharpoons H_2 \; ; \; E^\circ = -0.41 \text{ volts}$$

$$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-(1.0 \times 10^{-7}M) \; ; \; E^\circ = +0.82 \text{ volts}$$

$$Cl_2 + 2e \rightleftharpoons 2Cl^- \; ; \; E^\circ = +1.36 \text{ volts}$$

It is easily seen that it is far easier to get evolution of hydrogen at the cathode in preference to sodium. But hydrogen needs some activation energy in order to go over to the molecular form on mercury surface. This is what physical chemists say that hydrogen has a high overvoltage on mercury. On the other hand sodium is released on mercury quite readily. So the effective result is that contrary to what reduction potentials indicate we find that sodium is released on mercury cathode in preference to hydrogen. The sodium-mercury amalgam is treated with water when hydrogen is evolved and sodium hydroxide is formed. Again the electrode potentials indicate that we should get evolution of oxygen at the anode instead of chlorine. Once again oxygen has a high overvoltage on carbon (graphite). So chlorine is given out in preference to oxygen.

In the Nelson method no sodium is released on the perforated steel cathode. Instead hydrogen is liberated on the cathode. This makes the surrounding of the cathode rich in OH^- ions which combine with Na^+ ions to form NaOH solution.

Table 15.2. A Comparative study of the Different Methods of Preparation of Sodium Hydroxide

Method	Reaction	Temperature	Short Description	Remarks
1. Causticising	$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$	~ 80°C	20% aqueous solution of Na_2CO_3 is reacted with $Ca(OH)_2$ at ~80°C. The precipitated $CaCO_3$ is removed and excess water is removed by distillation. Finally the concentrated solution is dried in iron pans to get solid NaOH.	The by-product $CaCO_3$ is heated to get quick-lime CaO. An aqueous slurry of this may be reused in the process.
2. Electrolysis (*a*) Castner-Kellner Method	(*a*) $NaCl \rightarrow Na^+ + Cl^-$ $H_2O \rightarrow H^+ + OH^-$ *at the anode* : $2Cl^- \rightarrow Cl_2 \uparrow \; + 2e$ *at the cathode* : $Na^+ + e \rightarrow Na$ $(2Na + 2H_2O \rightarrow 2NaOH + H_2)$		(*a*) The electrolytic cell is divided into three compartments by slate partition. Saturated aqueous NaCl i.e. brine is used as the electrolyte. In the two side compartments hanging carbon rods function as anodes. Enough mercury is placed on the floor of the middle and the side compartments to serve as cathode. In some cells some hanging iron rods are used as cathodes in the middle compartments instead of mercury. As a result of electrolysis metallic sodium deposits over mercury and forms sodium amalgam. The cell is tilted and the amalgam is taken out. On treatment with water NaOH is obtained in solution. The solution is dried up to get solid NaOH. The mercury is reused.	This method produces two important by-products namely chlorine and hydrogen. Both these products are very useful for commercial preparations of other important chemicals.

Table 15.2. (Continued)

Method	Reaction	Temperature	Short Description	Remarks
(b) Nelson Method	$NaCl \rightarrow Na^+ + Cl^-$ $H_2O \rightarrow H^+ + OH^-$ *at the anode* : $2Cl^- \rightarrow Cl_2 \uparrow + 2e$ *at the cathode* : $2H^+ + 2e \rightarrow H_2$ $Na^+ + OH^- \rightarrow NaOH$	Steam	A perforated 'U' shaped steel vessel is used as the cathode. This is lined on the inside by an asbestos diaphragm. This 'U' shaped cathode is placed inside a rectangular iron receptacle. Saturated NaCl is taken inside the 'U' shaped vessel. The iron chamber is provided with arrangement for injecting steam and exits for H_2 and NaOH. Inside the cathode chamber there is an exit tube for chlorine. Graphite rod suspended in NaCl serves as the anode while the 'U' shaped vessel itself acts as the cathode.	In this method also the two important by-products are chlorine and hydrogen.

Properties and uses of sodium hydroxide : It is a strong base and reacts vigorously with acidic compounds :

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \; ; \; 2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

It also reacts with amphoteric elements like zinc and aluminium :

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$$

It has varied uses in the manufacture of soap, paper, in the purification of petroleum and in the many laboratory reactions.

Sodium Carbonate : This is one other very important commercial product of sodium. It may be obtained by a variety of methods : (*a*) calcination of natural soda $Na_2CO_3NaHCO_3.2H_2O$ (*b*) conversion of NaCl by Le Blanc procedure (*c*) Solvay or ammonia-soda process and (*d*) via reaction of CO_2 and steam during electrolysis of brine. A comparative study of these different methods is presented in Table 15.3.

The compound crystallises with different molecules of water : $Na_2CO_3.10H_2O$; $Na_2CO_3.7H_2O$ and $Na_2CO_3.H_2O$. The decahydrate is the well-known washing soda. This is a salt of a weak acid and a strong base and is therefore hydrolysed in water to give an alkaline pH :

$$Na_2CO_3 + 2H_2O \rightarrow H_2CO_3 + 2NaOH$$

This reaction may also be viewed in the following light :

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-} \; ; \; H_2O \rightleftharpoons H^+ + OH^-$$

$$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3$$

Effectively therefore there is a decrease in the H^+ ion concentration of water which leads to alkaline pH.

On strong heating anhydrous Na_2CO_3 is obtained.

Uses : In household purposes it is used as washing soda. It has varied uses in industry in the manufacture of glass, soap, sodium hydroxide. It also finds enough use in the laboratory.

Sodium Bicarbonate : Its major method of preparation is by the Solvay process. Saturated NaCl solution is treated first with gaseous ammonia and then by carbon dioxide. Under the reaction conditions the solubility product of $NaHCO_3$ is exceeded and the compound crystallises :

$$NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3 \; ; \; NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$

In the laboratory this can be obtained by saturating an aqueous solution of Na_2CO_3 with CO_2.

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$

This, being a salt of a weak acid and a strong base, undergoes hydrolysis to give an alkaline pH :

$$NaHCO_3 + H_2O \rightarrow NaOH + H_2CO_3$$

On heating the solid $NaHCO_3$ it decomposes to give Na_2CO_3, CO_2 and H_2O :

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

Table 15.3. A Comparative Study of the Different Methods of Preparation of Sodium Carbonate

Method	Reaction	Short Description	Remarks
1. From natural soda	$Na_2CO_3.NaHCO_3.2H_2O$ $\downarrow$ heat $Na_2CO_3 + CO_2 + H_2O$	Good deposit of sodium sesquicarbonate exists at Owens lake in California, at Magadi lake in East Africa and in some lakes in Egypt. The material is calcined to get rid of undesirable CO_2 and H_2O.	Since this natural deposit is concentrated in a few areas it can not compete more important synthetic methods.
2. Le Blanc Method	(*a*) $NaCl + H_2SO_4$ $\rightarrow NaHSO_4 + HCl$ $NaCl + NaHSO_4$ $\rightarrow Na_2SO_4 + HCl$ (*b*) $Na_2SO_4 + 2C$ $\downarrow$ 1000°C $Na_2S + 2CO_2$ $Na_2S + CaCO_3$ $\rightarrow Na_2CO_3 + CaS$ heat $\downarrow$ +water $\downarrow$ $\downarrow$ Na_2CO_3 solution Insoluble CaS $\downarrow$ heat Na_2CO_3	Common salt, NaCl, is first reacted with H_2SO_4 at red heat. HCl gas comes out as the by-product. Na_2SO_4 is powdered and mixed with coke and $CaCO_3$. The mixture is then fused and the fused mass extracted with boiling water The mixture is then filtered. Hydrated $Na_2CO_3.10H_2O$ crystals obtained from the filtrate is ignited to get anhydrous Na_2CO_3.	Two important by-products are HCl and CaS. The HCl gas is dissolved in water and sold as commercial quality HCl. The CaS is treated with water and CO_2 when H_2S and $CaCO_3$ are formed. The H_2S is heated in deficient supply of air to get sulphur and not SO_2; $CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$; $2H_2S + O_2 \rightarrow 2H_2O + 2S$. This method is practically obsolete now. It is in use for manufacture of Na_2SO_4.

Tabe 15.3. (Continued)

Method	Reaction	Short Description	Remarks
3. Solvay Method (Ammonia soda method)	(*a*) $NH_3 + H_2O + CO_2 \rightarrow NH_4^+ + HCO_3^-$ $NH_4HCO_3 + NaCl \rightarrow NaHCO_3 \downarrow + NH_4Cl$ (*b*) $2NaHCO_3 \xrightarrow{180°C} Na_2CO_3 + H_2O + CO_2$. (*c*) $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$	Saturated NaCl is allowed to drop into the ammonia absorption tower from the top while ammonia gas is forced up the tower. The ammoniacal brine is then allowed to trickle down the Solvay tower. Carbon dioxide gas is forced through the bottom up the tower in counter current principle. During the reactions in the Solvay tower the solubility product of $NaHCO_3$ is exceeded and crystals of sodium bicarbonate separate out. The solid sodium bicarbonate is calcined to get the sodium carbonate.	Carbon dioxide is obtained by heating $CaCO_3$. The quick lime so obtained is treated with water to have lime water $Ca(OH)_2$. The NH_4Cl is treated with $Ca(OH)_2$ to have the ammonia to be used in saturating the brine. The materials which are really spent are NaCl and $CaCO_3$. The final by-product is $CaCl_2$. The advantages are cheap and easily available raw materials and low fuel cost.
4. Electrolysis of brine	$NaCl \rightarrow Na^+ + Cl^-$ $H_2O \rightarrow H^+ + OH^-$ *at the anode* : $2Cl^- \rightarrow Cl_2 + 2e$ *at the cathode* : $2H^+ + 2e \rightarrow H_2$ $Na^+ + OH^- \rightarrow NaOH$ $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$	The procedure is an extension of the Nelson method. Brine is used as the electrolyte. Carbon rod is used as the anode inside the 'U' shaped perforated steel cathode. Here too an asbestos diaphragm is used on the inside of the steel cathode; steam and carbon dioxide are injected into the outer receptacle. The NaOH that is formed on the outside surface of the cathode reacts with CO_2 and Na_2CO_3 is formed.	Here too only two by-products namely hydrogen and chlorine are formed. Both these are of commercial importance. Chlorine is usually made use of in the manufacture of bleaching powder Ca(OCl)Cl. Hydrogen and chlorine are often utilised to make HCl. Nothing goes waste in this method.

Uses : Its major use is in medicine, in soft drinks and in baking powder. Baking powder consists of potassium hydrogen tartrate and sodium bicarbonate. The CO_2 that is liberated on heating the bread or cake dough makes them porous and thereby causing swelling.

Sodium Sulphate : Le Blanc process converts NaCl to Na_2CO_3. The first step in this conversion gives Na_2SO_4. The reaction between NaCl and H_2SO_4 is carried out around 1000°C when a coke of Na_2SO_4 and HCl gas are formed :

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$

The salt cake contains some undesirable H_2SO_4. The cake is reacted with steam and lime whereby insoluble $CaSO_4$ is formed :

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$$

The reaction mixture is filtered and the filtrate is cooled when crystals of Glauber's salt, $Na_2SO_4.10H_2O$, are obtained.

Uses : It finds good use in paper and glass industry.

Sodium Nitrate : It is mostly recovered from its natural source-Chile saltpetre. A saturated aqueous solution of Chile saltpetre is filtered and the filtrate is allowed to crystallise ($NaNO_3$). It is used as a fertiliser and in the manufacture of HNO_3.

Sodium Nitrite : This is obtained by the reduction of sodium nitrate with carbon. The released carbon dioxide is trapped by using lime in the reaction :

$$2NaNO_3 + C + Ca(OH)_2 \rightarrow 2NaNO_2 + CaCO_3 + H_2O$$

The salt is extremely soluble in water. It is in great demand in the manufacture of azo-dyes. In the laboratory also it finds enough use in the syntheses of many organic compounds.

Phosphates of Sodium : There are four different kinds of sodium phosphates. These are described below:

Disodium hydrogen phosphate : One mole proportion of phosphoric acid, H_3PO_4, is treated with two mole proportions of NaOH and the resulting solution is concentrated to get the crystals of $Na_2HPO_4.7H_2O$.

Sodium dihydrogen phosphate : Na_2HPO_4 and H_3PO_4 are mixed in 1 : 1 mole proportion and the solution concentrated to get the crystals of NaH_2PO_4.

Trisodium phosphate : Na_2HPO_4 is reacted with NaOH in hot water and the solution concentrated to get the crystals of Na_3PO_4.

Sodium ammonium hydrogen phosphate : NH_4Cl and Na_2HPO_4 is taken in hot water in 1 : 1 proportion and the solution concentrated. NaCl crystallises first and is removed. The remaining solution is concentrated to get the crystals of $NaNH_4HPO_44H_2O$. This compound is also known as *microcosmic salt*. On heating, the compound loses ammonia and water and is converted to sodium metaphosphate :

$$NaNH_4HPO_4 \rightarrow NaPO_3 + NH_3 + H_2O$$

Sodium metaphosphate is really hexa-metaphosphate $(NaPO_3)_6$ and is also known as *calgon* as it can remove calcium and magnesium of hard water as a complex phosphate :

$$Na_2[Na_4(PO_3)_6] + CaSO_4 \rightarrow Na_2[Na_2Ca(PO_3)_6] + Na_2SO_4$$

Sodium metaphosphate obtained by heating microcosmic salt in a platinum loop gives a clear bead. This combines with some coloured transition metal salts to give characteristic coloured beads known as microcosmic beads :

$$NaPO_3 + CoO \rightarrow NaCoPO_4 \text{ (blue)}$$
$$NaPO_3 + FeO(\text{from } FeSO_4) \rightarrow NaFePO_4 \text{ (green)}$$

Sodium Cyanide : This is obtained by the reaction of metallic sodium and ammonia gas around 700°C in a covered vessel. From time to time charcoal powder is added. The reaction proceeds via sodamide, cyanamide and finally gives cyanide :

$$2NH_3 + 2Na \rightarrow 2NaNH_2 + H_2 \text{ ; } 2NaNH_2 + C \rightarrow Na_2NCN + 2H_2$$
$$Na_2NCN + C \rightarrow 2NaCN$$

Sodium cyanide reacts with ferrous salts to give sodium ferrocyanide :

$$FeSO_4 + 6NaCN \rightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$

Sodium cyanide finds use as a complexing agent in electroplating of articles. In copper-, silver-, gold- and cadmium plating the salts of these metal ions are treated with cyanide whereby cyano complexes are formed. Electrodeposition from these baths on the cathode articles is slow, smooth and coherent.

Sodium Chloride : Sea water is the major source of common salt. Sea water is concentrated under the sun and the crude NaCl alongwith $MgCl_2$, etc. is crystallised. This is dissolved in water and treated with HCl gas when pure NaCl crystallises out first under the influence of common ion. The more soluble $MgCl_2$, $CaCl_2$ are retained in solution.

15.4.2. Industrial Preparation of Sodium : A comparative study of the two methods (*a*) Castner process and (*b*) Downs process is presented in Table 15.4.

We have already observed that sodium is a very reactive metal. Its reactivity is predicted by its low ionisation potential and very negative reduction potential. It is a soft shining metal which is lighter than water (density 0.97). Its melting and boiling points are 98°C and 883°C respectively. In the gaseous state it is monomeric. Its specific heat at 0°C is 0.28 Cal/g°C. It is a fine conductor.

The metal reacts quite vigorously with air, halogens, phosphorus, sulphur etc. to produce oxides (Na_2O, Na_2O_2), halides (NaCl, NaBr, NaI), Na_3P, Na_2S. It reacts with hydrogen around 360°C to form NaH. On electrolysis of NaH hydrogen is liberated at the anode while sodium goes to the cathode :

$$NaH \rightarrow Na^+ + H^-$$
$$\textit{at the cathode} : Na^+ + e \rightarrow Na$$
$$\textit{at the anode} : 2H^- \rightarrow H_2 + 2e$$

Uses of Sodium : Metallic sodium finds enough use in the laboratory in the syntheses of many organic compounds. Sodium amalgam is a common reducing agent. Much of sodium is used in the preparation of tetraethyl lead. Ethyl chloride is reacted with an amalgam containing 20% sodium and lead. Tetraethyl lead is used alongwith petrol or gasolin in automibile engines to increase efficiency.

Table 15.4. A Comparative Study of the Different Methods of Preparation of Sodium

Method	Reaction	Short Description	Remarks
1. Castner process of electrolysis	electrolyte : fused NaOH $NaOH \rightarrow Na^+ + OH^-$ *at the cathode* : $Na^+ + e \rightarrow Na$ *at the anode* : $4OH^- \rightarrow 2H_2O + O_2\uparrow + 4e$ $H_2O \rightleftharpoons H^+ + OH^-$ *at the cathode* : $2H^+ + 2e \rightarrow H_2\uparrow$ *at the anode* : $4OH^- \rightarrow 2H_2O + O_2\uparrow + 4e$	Fused NaOH is taken in a rectangular iron tank. The NaOH is kept in a fused state by a ring of gas burners. A copper or iron rod is pushed inside the tank. This serves as the cathode. The cathode is surrounded by nickel plate. The top of the cathode is surrounded by steel net. The anode and the cathode chambers are provided with outlets for the evolved oxygen and hydrogen. The sodium evolved at the cathode is collected with a perforated ladle and stored under kerosene.	The raw material is not available in nature. Much of the electric current is wasted in the electrolysis of H_2O. However not much heat is necessary. There is not much demand for oxygen.
4. Electrolysis of fused NaCl Downs process	$NaCl \rightarrow Na^+ + Cl^-$ *at the cathode* : $Na^+ + e \rightarrow Na$ *at the anode* : $2Cl^- \rightarrow Cl_2 + 2e$	Sodium chloride is mixed with KCl and KF and fused when the melting point gets lowered from ~ 800°C to ~ 600°C. The fused electrolyte is taken in an iron vessel. Graphite anode is introduced through the bottom of the iron vessel. The graphite anode is surrounded by iron or copper plates which serve as cathode. The chlorine at the anode is led out through a porcelain tube. The anode and the cathode are separated by a wire netting in order to minimise mixing of the materials evolved at the cathode and anode. Sodium liberated at the cathode is taken through a covering out of the cell. The sodium is then tapped out and finally stored under kerosene.	Consumption of electricity is low as there is only one electrolytic reaction. Chlorine as a by-product is very valuable.

15.5. POTASSIUM

Sodium and potassium are closely related in their chemical behaviour. Potassium is even more reactive than sodium. A few selected compounds are described below:

15.5.1. Some Compounds of Potassium : Preparations of a few compounds are a little bit different from their sodium analogues.

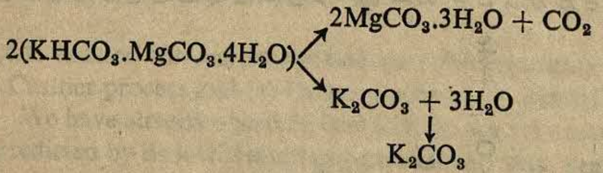
Potassium carbonate and bicarbonate : We have already seen that sodium bicarbonate can be easily prepared by the Solvay method because in the Solvay tower the solubility product of sodium bicarbonate is exceeded when saturated brine reacts with ammonium bicarbonate. But in the case of potassium its bicarbonate is quite soluble and hence potassium bicarbonate does not easily separate out. A different method is therefore has to be followed.

Hydrated magnesium carbonate is added to a cold and saturated solution of KCl and the whole mixture is then treated with CO_2. This leads to the formation of sparingly soluble double salt of potassium magnesium hydrogen carbonate. This is collected and heated with water. Magnesium carbonate separates out and carbon dioxide is evolved. These two products can be used over and over again. The mixture is next filtered and concentrated when potassium carbonate crystallises out :

$$MgCO_3.3H_2O + CO_2 \rightarrow Mg(HCO_3)_2 + 2H_2O$$

$$2KCl + Mg(HCO_3)_2 \rightarrow 2KHCO_3 + MgCl_2$$

$$KHCO_3 + MgCO_3.3H_2O + H_2O \rightarrow KHCO_3.MgCO_3.4H_2O$$



$$2(KHCO_3.MgCO_3.4H_2O) \begin{cases} \nearrow 2MgCO_3.3H_2O + CO_2 \\ \searrow K_2CO_3 + 3H_2O \\ \qquad \downarrow \\ \qquad K_2CO_3 \end{cases}$$

Potassium bicarbonate : This is formed when an aqueous solution of K_2CO_3 is saturated with CO_2 :

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3$$

Both $KHCO_3$ and K_2CO_3 undergo hydrolysis and show alkaline pH.

Potassium Chloride : Natural carnallite is $KCl.MgCl_2.6H_2O$. This is dissolved in hot water to get a saturated solution. On cooling the less soluble KCl crystallises out while $MgCl_2$ is retained in solution. The crude KCl thus obtained is further purified by recrystallisation from hot water.

Potassium Cyanide : This is obtained by passing ammonia gas over a mixture of K_2CO_3 and carbon.

$$K_2CO_3 + C + 2NH_3 \rightarrow 2KCN + 3H_2O$$

Potassium ferrocyanide may also be decomposed by the action of potassium metal :

$$K_4[Fe(CN)_6] + 2K \rightarrow 6KCN + Fe$$

The reaction mixture is extracted with water and pure potassium cyanide is recovered from the filtrate. Sodium cyanide may also be prepared by a similar procedure.

Potassium Thiocyanate : This is obtained either (*a*) by fusing $K_4[Fe(CN)_6]$ with sulphur or (*b*) by fusing KCN with sulphur :

$$K_4[Fe(CN)_6] + 4S \rightarrow 4KSCN + Fe(CN)_2$$

$$KCN + S \rightarrow KSCN$$

Potassium Iodide : Iodine is made to react with a hot aqueous solution of KOH :

$$3I_2 + 6KOH \rightarrow 5KI + KIO_3 + 3H_2O$$

The solution is dried up and heated with little charcoal to reduce the iodate :

$$2KIO_3 + 3C \rightarrow 2KI + 3CO_2$$

Pure KI is obtained by recrystallisation of the crude product from water. It is of frequent use in the laboratory in iodometric estimations.

Potassium Nitrate : Double decomposition is carried out between aqueous solutions of $NaNO_3$ and KCl. NaCl crystallises first. The filtrate is concentrated to get KNO_3. It finds use as a fertiliser, as an explosive and in glass industry.

15.5.2. Industrial Preparation of Potassium : The methods of its extraction are parallel to those used for sodium. Its properties are also similar to those of sodium.

EXERCISES

1. It is said that the chemistry of the alkalies is basically the chemistry of their ions. Do you agree?

2. What do you understand by diagonal relationship? Give an account of the chemistry of any one pair of elements showing such relationship.

3. Lithium has several points of similarities and several points of dissimilarities with the remaining alkalies. Bring these out.

4. Give an account of the preparation, properties and uses of the following compounds : (*a*) sodium carbonate (*b*) sodium nitrite (*c*) sodium ammonium hydrogen phosphate (*d*) potassium cyanide (*e*) potassium bicarbonate (*f*) potassium iodide (*g*) potassium ferrocyanide

5. Starting from sodium chloride how can you prepare sodium carbonate by the Solvay method? Can this method be applied to potassium carbonate?

6. Starting from sea water how can we get pure sodium chloride?

7. How would you obtain lithium metal from one of its natural source?

8. State with equations the reactions that take place in the following cases :

(*a*) aluminium is heated with concentrated NaOH

(*b*) a piece of potassium metal is dropped into water and another in kerosine

(*c*) fused NaCl is electrolysed

(*d*) brine is electrolysed in multi chambered cell with running mercury serving as cathode while carbon rods act as anodes.

(*e*) hydrochloric acid is added to a solution of sodium chloride

(*f*) electrolysis of fused lithium hydride

9. What volume of 0.5*M* HCl will be required to neutralise (*a*) 1.06 gram of Na_2CO_3 and (*b*) 1.06 gram $NaHCO_3$ (answer : (*b*) 25.2 ml)

CHAPTER 16

GROUP IIA : MAGNESIUM AND THE ALKALINE EARTHS

16.1. INTRODUCTION

Group IIA of the periodic table contains the elements : beryllium, magnesium, calcium, strontium, barium and radium. Of these calcium, strontium and barium are known as the family of the alkaline earths. All these elements have two electrons in the outermost *ns* shell. The alkaline earths have a chemistry which is largely that of their ions. We shall begin with a comparative study of the chemistry of these elements, which will be followed by an account of the salient features of the chemistries of magnesium and the alkaline earths.

16.2. A COMPARATIVE STUDY OF THE CHEMISTRY OF THE GROUP IIA ELEMENTS

In this discussion we will not attach much importance to the chemistries of beryllium and radium. The chemistry of radium alongwith two other radioactive elements thorium and uranium is included in a later group.

Physical Properties : 1. All these elements belong to the family of representative elements and have two electrons over a noble gas electronic configuration. Thus their inclusion in group IIA is justified.

2. The ionisation potentials of these elements are low and decrease down the group with increasing atomic number. This indicates their ready tendency to give up the valence electrons. However for the two valence electrons there will be two ionisation potentials.

Table 16.1. A Comparison of some Properties of Group IIA Elements

Element	Atomic Number	Electron Configuration	Ionisation Potential	Electronegativity	Ionic Radius (A) (M^{2+})	Reduction Potential $M^{2+} + 2e \rightleftharpoons M$(volts)	M.P. (°C)
Be	4	[He] $2s^2$	9.32 ; 18.20	1.5	0.31	-1.85	1284
Mg	12	[Ne] $3s^2$	7.64 ; 15.03	1.2	0.65	-2.37	651
Ca	20	[Ar] $4s^2$	6.11 ; 11.87	1.0	0.99	-2.87	851
Sr	38	[Kr] $5s^2$	5.69 ; 11.02	1.0	1.10	-2.89	770
Ba	56	[Xe] $6s^2$	5.21 ; 10.00	0.9	1.29	-2.90	710
Ra	88	[Rn] $7s^2$	5.27 ; 10.14	0.9	1.50	-2.92	960

3. As we go down the group the sizes of the bipositive cations continue to increase. With incresing atomic number in the same group electrons are added to new quantum shells.

4. The electronegativities of these elements is rather low compared to that of fluorine. As expected electronegativities decrease slowly down the group.

5. The reduction potentials of these elements are negative and become increasingly negative with increasing atomic number. This once again reminds us that the elements are becoming more and more basic i.e. metallic in their character with increasing atomic number.

6. In this group beryllium is the smallest in size but its charge is the same as the other members. Therefore according to Fajans' rules beryllium is likely to be the most complex forming and barium and radium the least.

Chemical Properties : 1. If we leave aside beryllium and radium then according to Fajans' rules magnesium may show some slight covalent properties but the other three members are likely to show mostly ionic character. Tendency of complex formation is not high in magnesium but indeed very low in the alkaline earths.

2. Magnesium and the alkaline earths readily react with water to evolve hydrogen and form hydroxides in solution :

$$M + 2H_2O \rightarrow M(OH)_2 + H_2$$

All these elements react with oxygen of air to give the oxides MO. They are also known to react with steam to form MO and liberate hydrogen.

3. Calcium, strontium, and barium react with hydrogen in the temperature range 200-400°C to form their hydrides. These hydrides belong to the class of ionic hydrides as is revealed by the evolution of hydrogen at the anode on electrolysis of their fused halides :

$$CaH_2 \rightarrow Ca^{2+} + 2H^-$$

at the cathode : $Ca^{2+} + 2e \rightarrow Ca$

at the anode : $2H^- \rightarrow H_2 + 2e$

4. They also react vigorously with halogens to form their halides. The reactivity increases with increasing atomic number. The halides are true ionic compounds.

5. Magnesium gives monoxide and peroxide while the alkaline earths can go upto the superoxide : MO, MO_2 and $M(O_2)_2$.

6. That these elements are somewhat less ionic than the alkalies in group IA is nicely demonstrated by the fact that while the alkalies give salts of bicarbonates, bisulphites and polyhalides in the solid crystalline state the alkaline earths are known to produce these salts in solution only. It is a common-place knowledge that on the passage of excess CO_2 through a suspension of $CaCO_3$ it dissolves to give soluble $Ca(HCO_3)_2$ but attempts to concentrate and crystallise the bicarbonate leads to its decomposition to the carbonate.

16.3. MAGNESIUM

16.3.1. Some Compounds of Magnesium : Preparation and properties of some compounds of magnesium are given below:

Magnesium Oxide and Hydroxide : Burning magnesium metal in air furnishes MgO. This can also be produced by thermal decomposition of $MgCO_3$:

$$MgCO_3 \rightarrow MgO + CO_2$$

The oxide has a high melting point (1800°C). Because of its heat resistance electric furnaces are often made of bricks of MgO. It also finds use as an antacid.

Magnesium hydroxide is sparingly soluble in water. On the addition of NH_4OH to any soluble magnesium salts a precipitate of $Mg(OH)_2$ is obtained. However in the presence of a common ion in the form of NH_4Cl dissociation of NH_4OH is considerably suppressed. As a result NH_4OH is rendered a still weaker base and the solubility product of $Mg(OH)_2$ is not exceeded and hence $Mg(OH)_2$ is not precipitated. This principle is utilised in keeping magnesium ion in solution in the qualitative scheme of analysis of metal ions.

Magnesium Chloride : This is found in nature in the form of carnallite $KCl.MgCl_2.6H_2O$. This product is dissolved in water and fractionally crystallised. KCl being comparatively less soluble crystallises first while the more soluble $MgCl_2$ is retained in solution. The filtrate is concentrated and $MgCl_2.6H_2O$ crystals are collected. This hydrated chloride cannot be dehydrated by mere heating as a basis chloride is formed :

$$MgCl_2.6H_2O \xrightarrow{\text{heat}} Mg(OH)Cl + HCl + 5H_2O$$

The hydrolysis can be checked if heated in an atmosphere of HCl gas :

$$MgCl_2.6H_2O \xrightarrow[\text{HCl gas}]{\text{heat}} MgCl_2 + 6H_2O$$

Sorel Cement or Zyolith : Magnesium carbonate is decomposed to MgO and CO_2 on strong heating : $MgCO_3 \rightarrow MgO + CO_2$. Incompletely decomposed material consists of $MgCO_3$ and MgO. This material when added to a concentrated solution of $MgCl_2$ gives a thick paste which sets within a short time to a hard cement-like mass. The mixture of $MgCO_3$, MgO and $MgCl_2$ is known as Sorel cement or Zyolith. This finds use in white polish, in filling tooth cavities and in replacements of tiles.

Magnesium Sulphate : As can be guessed this salt can be obtained by the action of sulphuric acid on $MgCO_3$, MgO or magnesium metal. The resulting solution on crystallisation gives the heptahydrate : $MgSO_4.7H_2O$. This is a true vitriol and is also known as Epsom salt. It forms a schonite type double sulphate with K_2SO_4 : $K_2SO_4.MgSO_4.6H_2O$. It is used in the making of soap, cotton and medicines.

Magnesium Carbonate : This compound occurs in nature as magnesite ($MgCO_3$) and as dolomite ($MgCO_3.CaCO_3$). In the laboratory this can be prepared by double decomposition between a soluble magnesium salt and sodium carbonate. However this precipitate also contains some $Mg(OH)_2$ formed via hydrolysis of Na_2CO_3. In order to get pure $MgCO_3$ the above precipitate is treated with excess of CO_2 when soluble magnesium bicarbonate is formed. On heating this solution pure $MgCO_3$ is precipitated as a fine powder :

$$\begin{tikzcd}
2MgCl_2 + 2Na_2CO_3 + H_2O \rightarrow MgCO_3.Mg(OH)_2 + 4NaCl + CO_2 \arrow[d, "3CO_2 + H_2O"] \\
2(MgCO_3 + H_2O + CO_2) \leftarrow 2Mg(HCO_3)_2
\end{tikzcd}$$

The compound finds use in the preparation of cosmetics, tooth powder and medicine.

Magnesium Perchlorate : This salt is prepared by the reaction of magnesium carbonate with perchloric acid ($HClO_4$). The solid anhydrous $MgClO_4$ is a very effective dehydrating agent known as *anhydrone*. The hydrated salt can be brought back to the anhydrous form by heating to 150°C.

Magnesium Phosphates : There are several magnesium phosphates. This is because of the fact that phosphoric acid, H_3PO_4, behaves under different experimental conditions as (*a*) monobasic (*b*) dibasic and (*c*) tribasic acid. Besides on heating some of the phosphates give pyro- and other types of condensed phosphates. A short resume of the more important magnesium phosphates is given below :

$$MgSO_4.7H_2O \xrightarrow{Na_2HPO_4 + NaHCO_3} Mg_3(PO_4)_2 \downarrow$$

$$\xrightarrow{Na_2HPO_4} MgHPO_4.3H_2O \downarrow$$

$$MgO \xrightarrow{\text{hot concentrated } H_3PO_4} Mg(H_2PO_4)_2.2H_2O \downarrow$$

$$\begin{tikzcd}
MgSO_4 + NH_4Cl + NH_4OH \xrightarrow{\text{phosphate}} Mg(NH_4)PO_4.6H_2O \downarrow \arrow[d, "\text{heat}"] \\
Mg_2P_2O_7 + NH_3 + H_2O
\end{tikzcd}$$

(magnesium pyrophosphate)

16.3.2. Industrial Preparation of Magnesium: Although the element is found in nature in a variety of forms from commercial view point three important ores are the following : (*a*) magnesite, $MgCO_3$; (*b*) dolomite, $MgCO_3.CaCO_3$ and (*c*) carnallite KCl, $MgCl_2.6H_2O$. In Chapter 13 we have given a general resume of the different methods of extraction of metals. We have seen that usually electrolytic method has to be resorted to for the extraction of those metals whose reduction potentials are more negative than −1.66 volts. Thus for magnesium (reduction potential being −2.37 volts) electrolytic procedure is an obvious choice. However the metal has also been obtained by carbon reduction of its oxide when the equilibrium is favourably shifted towards the metal by controlling reaction conditions:

Electrolysis of fused $MgCl_2$: The melting point of $MgCl_2$ is 750°C. Usually fused $MgCl_2$ is taken in a rectangular steel vessel which serves as the cathode. A graphite rod is suspended into the fused electrolyte. The graphite anode is enclosed into a porcelain tube with an exit for chlorine. The steel vessel is provided with an inlet and outlet for a reducing gas like hydrogen or coal-gas in order to protect the metal from possible oxidation.

at the cathode : $Mg^{2+} + 2e \rightarrow Mg$

at the anode : $2Cl^- \rightarrow Cl_2 + 2e$

The magnesium metal floats up and is removed.

Magnesium can also be extracted from sea water. Sea water is concentrated under the sun and then treated with $Ca(OH)_2$. Magnesium chloride is precipitated as $Mg(OH)_2$. The precipitate is collected and converted to $MgCl_2.6H_2O$. This is dehydrated in an atmosphere of dry HCl gas. The anhydrous $MgCl_2$ is fused and electrolysed to get magnesium at the cathode.

Carbon reduction of Magnesium Oxide : This is rather an unusual method for a metal with such a high negative reduction potential. The reduction reaction attains an equilibrium and conditions are so regulated that it is favoured towards

$$MgO + C \rightleftharpoons Mg + CO$$

reduction. In practice fine powder of MgO and coke are mixed to form small pellets and these pellets are fed into an electric furnace operating around 2000°C. At this temperature the above equilibrium is shifted towards the right and gaseous magnesium and carbon monoxide are led out of the furnace. The gaseous mixture is rapidly cooled by natural gas (mainly CH_4) when magnesium (boiling point 1100°C) is converted to the liquid state. This is further distilled to get pure magnesium.

Magnesium is a silvery white metal. Its density is 1.75. It burns in air with a bright flame. It reacts quite vigorously with many nonmetals like oxygen, nitrogen, arsenic, sulphur etc. It also reacts with boron and silicon to form magnesium boride and silicide

$$2Mg + O_2 \rightarrow 2MgO \quad ; \quad 3Mg + N_2 \rightarrow Mg_3N_2$$
$$3Mg + 2B \rightarrow Mg_3B_2 \quad ; \quad 2Mg + Si \rightarrow Mg_2Si$$

Uses : Its alloys are light but at the same time tough. Magnesium (2%) and aluminium (98%) alloy is used in the manufacture of different parts of aircrafts and automobiles. It finds use in the manufacture of fireworks and flashbulbs etc. In the laboratory one of its most important uses is in the preparation of Grignard reagents (CH_3MgBr, CH_3MgI etc).

16.4. CALCIUM

16.4.1. Some Compounds of Calcium : Some of the compounds of this metal are of vital commercial importance. Limestone is one of the most sought after industrial raw materials which is needed in one or more stages in the manufacture of materials like cement, glass, steel, calcium cyanamide and so on (Fig 16.1). Given below is a flowsheet of such preparations. It is in great demand as a flux material.

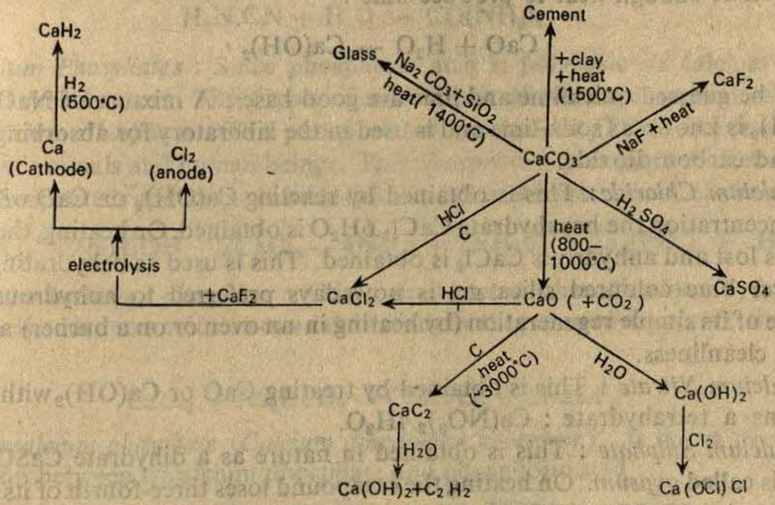


Fig. 16.1. Flowsheet of the syntheses of different compounds of calcium starting from limestone ($CaCO_3$)

Calcium Hydride (*Hydrolith*) : Calcium metal reacts with hydrogen around 500°C to produce calcium hydride. This compound is a typical ionic hydride. On electrolysis calcium is deposited at the cathode while hydrogen is liberated at the anode :

$$\text{at the cathode : } Ca^{2+} + 2e \rightarrow Ca$$

$$\text{at the anode : } 2H^- \rightarrow H_2 + 2e$$

The compound reacts vigorously with water to give calcium hydroxide alongwith evolution of hydrogen :

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

Calcium oxide (*Quicklime*) : Natural limestone on heating gives quicklime and CO_2. The reaction is exothermic and attains equilibrium :

$$CaCO_3 \rightleftharpoons CaO + CO_2 + 42.5 \text{ KCal}$$

In order to take the reaction to a fruitful end the evolved CO_2 has to be removed from the reaction zone. The reaction is carried out in a lime kiln. A lime kiln is usually wider in girth towards the bottom but gradually narrows out at the top. Near the lower end there are two openings : through one producer gas obtained by burning coal in air ($CO + N_2$) is introduced while through the other opening the burnt out quicklime is drawn out. At the top again there are two openings : through a side opening limestone is introduced from time to time and through the other the spent gases are allowed to escape. Burning of limestone is thus a continuous process. Inside the lime kiln the temperature is kept around 800-1000°C and the CO_2 is allowed to escape through the top opening so that the reaction proceeds to completion.

Quicklime has a melting point 2570°C. It reacts vigorously with water with evolution of enough heat to produce lime :

$$CaO + H_2O \rightarrow Ca(OH)_2$$

As can be guessed quicklime and lime are good bases. A mixture of NaOH and $Ca(OH)_2$ is known as soda-lime and is used in the laboratory for absorbing moisture and carbon dioxide.

Calcium Chloride: This is obtained by reacting $Ca(OH)_2$ or CaO with HCl. On concentration the hexahydrate $CaCl_2.6H_2O$ is obtained. On heating, the crystal water is lost and anhydrous $CaCl_2$ is obtained. This is used as dehydrating agent. However blue coloured silica gel is nowadays preferred to anhydrous $CaCl_2$ because of its simple regeneration (by heating in an oven or on a burner) and also for its cleanliness.

Calcium Nitrate : This is obtained by treating CaO or $Ca(OH)_2$ with HNO_3. It forms a tetrahydrate : $Ca(NO_3)_2.4H_2O$.

Calcium Sulphate : This is obtained in nature as a dihydrate $CaSO_4.2H_2O$ which is called *gypsum*. On heating the compound loses three-fourth of its hydrate water to give $(CaSO_4)_2.H_2O$ (also written as $CaSO_4.\frac{1}{2}H_2O$). During dehydration gypsum is heated in large steel pots and is stirred mechanically. The hemihydrate is known as *Plaster of Paris*. On making a thick slurry with water it absorbs water and goes over to the form $CaSO_4.2H_2O$. During this rehydration it becomes very hard. This property has made *Plaster of Paris* an ideal substance for making medical orthopaedic bandage, moulds of different types and also in sculpture work. Gypsum is also used in the synthesis of the important fertiliser $(NH_4)_2SO_4$ via reaction of $CaSO_4.2H_2O$ and $(NH_4)_2CO_3$. It also finds use in paper industry as a binder.

Calcium Carbide: It is obtained by reacting quicklime and coke around 3000°C :

$$CaO + 3C \rightarrow CaC_2 + CO$$

The reaction is carried out in an electric arc furnace. The mixture of quicklime and coke is introduced from the top while the molten calcium carbide is drawn out through a hole at the bottom side. Electric arc is set between two carbon electrodes. The high temperature and the arc force the coke to react with quicklime to give the carbide. The carbide is drawn out of the furnace in liquid state and is then cooled. The compound reacts with water to produce acetylene :

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

Calcium Cyanamide : Freshly prepared calcium carbide is reacted with nitrogen at 1000°C when the cyanamide is formed :

$$CaC_2 + N_2 \rightarrow CaNCN + C$$

The black coloured reaction mixture as obtained above is called *nitrolim*. This is used as fertiliser. In the soil calcium cyanamide comes in contact with water and carbon dioxide of air and is finally transformed into urea :

$$CaNCN + H_2O + CO_2 \rightarrow CaCO_3 + H_2N.CN$$
$$H_2N.CN + H_2O \rightarrow CO(NH_2)_2$$

Calcium Phosphates : Since phosphoric acid is polybasic its calcium salts are also of varied nature. Three types of calcium phosphates are described below.

Tricalcium Phosphate : This phosphate of calcium, $Ca_3(PO_4)_2$, is present in the bone of animals and human beings. This phosphate is precipitated when some sodium phosphate is added to a soluble calcium salt in the presence of ammonia :

$$2Na_2HPO_4 + 2NH_4OH + 2CaCl_2 \rightarrow 4NaCl + 2NH_4Cl + Ca_3(PO_4)_2 + 2H_2O$$

Calcium hydrogen phosphate : This is precipitated when disodium hydrogen phosphate is added to a solution of a calcium salt in the presence of a small amount of acid :

$$CaCl_2 + Na_2HPO_4 \rightarrow CaHPO_4 + 2NaCl$$

Monocalcium phosphate (*Calcium dihydrogen phosphate*) : It is the result of the reaction between tricalcium phosphate and phosphoric acid :

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$$

This calcium phosphate is quite soluble compared to the two other phosphates described earlier. Because of this solubility it is a good fertiliser.

On commercial scale it is marketed as *superphosphate of lime* to be used as fertiliser. Natural phosphate rock ore is mechanically stirred with sulphuric acid of moderate strength :

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 2H_2O \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4.2H_2O$$

The product mixture consisting of $Ca(H_2PO_4)_2$ and $CaSO_4.2H_2O$ goes by the name *superphosphate of lime*. During the manufacture gases like HF, CO_2 and SiF_4 are evolved because of the other constituents present in the natural phosphate rocks.

Portland Cement : The term cement is now a household knowledge. In these days of modern civilisation we cannot conceive of living without this very essential building material. This is used in all sorts of construction beginning from a small dwelling house to all complicated multistoried buildings, bridge, dam, barrage, industries so on and so forth. The colour of cement is light ash and resembles very much that of a stone found in Portland in England. It is not a single chemical but a mixture of several complex aluminosilicates. The major constituents are tricalcium silicate ($3CaO.SiO_2$), calcium orthosilicate ($2CaO.SiO_2$) and tricalcium aluminate ($3CaO.Al_2O_3$). Besides these major constituents there are present two other complex products : a complex calcium aluminate ($12CaO.7Al_2O_3$) and a complex aluminoferrate ($4CaO.Al_2O_3.Fe_2O_3$).

The major raw materials for the manufacture of cement are limestone ($CaCO_3$) and clay. The quality of these raw materials should be such that there is present sufficient silica to give the necessary silicates in the final reaction product. The firing of the raw materials is done in a very special type of furnace called *Rotary Kiln*. Depending on the output quantity the size has to vary. A rotary kiln may vary in length from 150 to 350 feet and in diameter from 8 to 14 feet. The kiln is placed in an inclined position (Fig. 16.2) and the entire kiln is slowly rotated by electrically driven motor. A thick slurry is made of limestone and clay and is dropped down an opening at the top end of the kiln. The mixture rolls down the rotating kiln and is subjected to gradually increasing temperature. At the bottom firing end a huge flame of around 40 feet is forced in by a pulverised coal burner. As the slurry rolls down, the flame and the heat roast the slurry to cement clinkers. At the firing end the temperature may reach 1500°C. At the bottom end the cement clinkers assume the proportion of marbles and are drawn out into a cooler. The cement marbles are then ground in ball-mills to a fine dust.

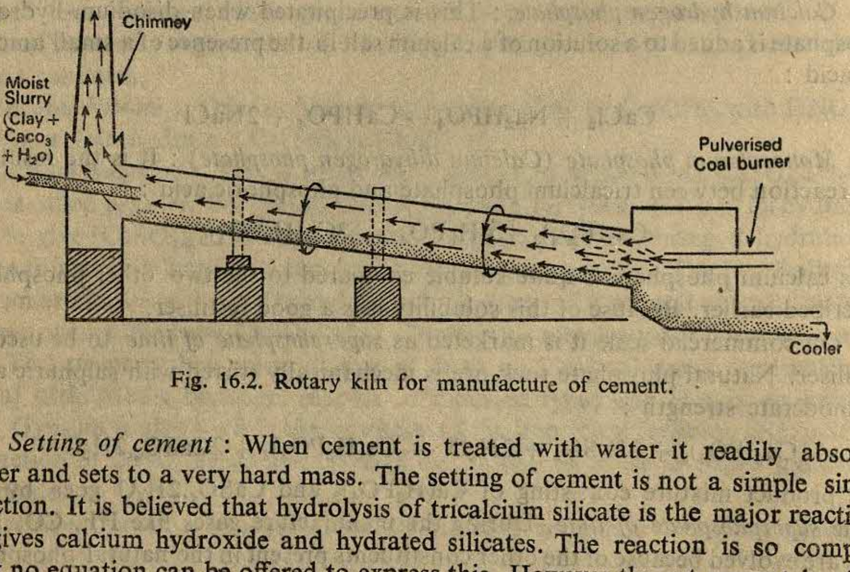


Fig. 16.2. Rotary kiln for manufacture of cement.

Setting of cement : When cement is treated with water it readily absorbs water and sets to a very hard mass. The setting of cement is not a simple single reaction. It is believed that hydrolysis of tricalcium silicate is the major reaction. It gives calcium hydroxide and hydrated silicates. The reaction is so complex that no equation can be offered to express this. However the set cement is often expressed as $3CaO.Al_2O_3.6H_2O$ alongwith some complex silicates.

Concrete : In building construction cement, silica and stone chips are mixed in right proportion depending on the nature of the work and the mixture is treated with water. This slurry is used as a binding material. This mixture is known as *concrete*. This sets to a very hard mass of enormous strength. If this slurry is set around iron or steel rods this is known as *ferro-concrete or reinforced concrete*. The strength of reinforced concrete is even greater than ordinary concrete and is a common feature of construction of building roofs, pillars and columns of multi-storied buildings, dams, bridges etc.

Bleaching Powder : This is much too well known as a disinfectant and a bleaching agent. It is obtained basically by way of the following reaction :

$$Ca(OH)_2 + Cl_2 \rightarrow Ca(OCl)Cl + H_2O$$

The chlorine used in this reaction is usually obtained as a by-product of electrolytic reactions (eg. electrolysis of fused NaCl etc.). The reaction is carried out in a chamber provided with several horizontal racks. Slaked lime enters the chamber at the top and is forced by mechanical device to travel from one horizontal platform to another and so on. Chlorine is introduced through the bottom of the chamber and travels upwards. So there is a reaction of the down-coming slaked lime and the up-going chlorine according to the counter current principle. By the time the lime reaches the bottom of the chamber it is converted to the bleaching powder. The temperature during such reaction is maintained at 20-35°C.

Analysis shows that in bleaching powder CaO and Cl_2 are present in the ratio 1 : 1 Hence the formula is written as Ca(OCl)Cl. The bleaching powder available in the market always contains some slaked lime (unconverted $Ca(OH)_2$). It always smells of chlorine due to some decomposition. It reacts with boiling water to give calcium chlorate and calcium chloride :

$$6Ca(OCl)Cl \rightarrow Ca(ClO_3)_2 + 5CaCl_2$$

On reacting with acids chlorine gas is liberated :

$$Ca(OCl)Cl + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$$
$$Ca(OCl)Cl + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$$

With potassium iodide iodine is liberated (evidently the liberated chlorine oxidises the iodide ion) :

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

The real bleaching agent in bleaching powder is the chlorine. Cotton garments can be dependably bleached with bleaching powder. Cotton goods are first washed with washing soda and then left in a solution of bleaching powder for some hours. On washing with a solution of very dilute HCl or H_2SO_4 the excess chlorine is got rid of. Finally the goods are washed well with water.

16.4.2. Industrial Preparation of Calcium : Calcium is found in nature in a variety of forms : limestone ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$), anhydrite ($CaSO_4$), gypsum ($CaSO_4.2H_2O$), fluorspar (CaF_2) and phosphate rock ($Ca_3(PO_4)_2$).

None of the above materials is suitable for direct extraction of the metal. In practice the metal is extracted from its chloride salt. Following our discussion in Chapter 13 one can guess that the suitable method must be electrolysis. The electrolyte is fused anhydrous $CaCl_2$ containing 10% CaF_2. This brings down the temperature to within the range 600-700°C. The electrolytic cell is a graphite vessel through the bottom of which is circulated cold water to keep it as cool as possible. Inside the fused electrolyte is lowered two graphite anode rods and an iron cathode rod. The iron cathode rod is provided with arrangement for circulating cold water through it so that the deposited calcium metal may remain in solidified form. The cathode goes just a little below the surface of the fused electrolyte. As calcium continues to get deposited at the iron rod the cathode is gradually screwed up. The chlorine gas liberated at the graphite rods is led away through a chimney.

at the cathode : $Ca^{2+} + 2e \rightarrow Ca$

at the anode : $2Cl^- \rightarrow Cl_2 + 2e$

16.2. A Comparative Study of Strontium and Barium and their Compounds

Element/ Compound	Ore/Mineral	Method of Preparation	Properties	Uses
Strontium	Strontianite ($SrCO_3$) Celestine ($SrSO_4$)	(*a*) $SrCO_3 + 2HCl \rightarrow SrCl_2 + CO_2 + H_2O$ Electrolysis of fused $SrCl_2 + KCl$; deposition of strontium *at the cathode* ; $Sr^{2+} + 2e \rightarrow Sr$; *at the anode* : $2Cl^- \rightarrow Cl_2 + 2e$ (*b*) $SrSO_4 + 4C \rightarrow SrS + 4CO$ $SrS + 2NaOH \rightarrow Sr(OH)_2 + Na_2S$ $Sr(OH)_2 \rightarrow SrO + H_2O$ $SrO + 2HCl \rightarrow SrCl_2 + H_2O$ Electrolysis of $SrCl_2$ gives Sr.	Bright white $2Sr + O_2 \rightarrow 2SrO$ $Sr + 2H_2O \rightarrow Sr(OH)_2 + H_2$ $Sr + 2HCl \rightarrow SrCl_2 + H_2$ $3Sr + N_2 \rightarrow Sr_3N_2$ M.P. 770°C B.P. 1320°C	The metal has very little demand,
Strontium Hydride(SrH_2)		$Sr + H_2 \xrightarrow{heat} SrH_2$	On electrolysis of SrH_2 in another fused salt hydrogen is given off at the anode. *cathode* : $Sr^{2+} + 2e \rightarrow Sr$ *anode* : $2H^- \rightarrow H_2 + 2e$	
Strontium Oxide (SrO) and peroxide (SrO_2)		$2Sr + O_2 \rightarrow 2SrO$ $2SrO + O_2 \rightarrow 2SrO_2$ $SrCO_3 \xrightarrow{heat} SrO + CO_2$	$SrO + H_2O \rightarrow Sr(OH)_2$ $Sr(OH)_2 + CO_2 \rightarrow SrCO_3 + H_2O$	
Strontium Sulphate ($SrSO_4$)		Occurs in nature. (*a*) $SrO + H_2SO_4 \rightarrow \downarrow SrSO_4 + H_2O$ (*b*) $SrCl_2 + H_2SO_4 \rightarrow \downarrow SrSO_4 + 2HCl$	Insoluble in water and hence it is precipitated during chemical reaction.	

Table 16.2. (Continued)

Element/ Compound	Ore/Mineral	Method of Preparation	Properties	Uses
Barium	Heavy spar ($BaSO_4$) witherite ($BaCO_3$)	The sulphate is reacted with carbon to Ba S. This is converted to $Ba(OH)_2$ which is then changed to anhydrous $BaCl_2$. Usually electrolysis of anhydrous $BaCl_2$ is carried out using mercury cathode. The amalgam is then distilled to remove mercury.	Soft and white. M.P. 710°C B.P. 1500°C ; $2Ba + O_2 \rightarrow 2BaO$ $Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2$ All other reactions are parallel to those of strontium	
Barium Hydride (BaH_2)		$Ba + H_2 \xrightarrow{\text{heat}} BaH_2$	Electrolysis of fused BaH_2 gives hydrogen at the anode	
Barium Oxide and Peroxide		$2Ba + O_2 \rightarrow 2BaO$ $2BaO + O_2 \rightleftharpoons 2BaO_2$ $BaCO_3 + C \xrightarrow{800°C} BaO + 2CO$	$BaO + H_2O \rightarrow Ba(OH)_2$ $Ba(OH)_2$ is strongly alkaline and is known as baryta	
Barium Chloride		$BaCO_3 + 2HCl \rightarrow BaCl_2 + CO_2 + H_2O$	Soluble in water	
Barium Sulphate		Occurs in nature as heavy spar $BaO + H_2SO_4 \rightarrow \downarrow BaSO_4 + H_2O$ $BaCl_2 + H_2SO_4 \rightarrow \downarrow BaSO_4 + 2HCl$	Insoluble in water	Quantitative analysis of barium and sulphate ions.

Properties : It is quite an active silvery white metal. Its melting and boiling points are 851° and 1440°C respectively. It is a soft metal with a density 1.55. Some reactions of the metal are :

$$2Ca + O_2 \rightarrow 2CaO \; ; \; Ca + H_2 \rightarrow CaH_2 \; ; \; Ca + Cl_2 \rightarrow CaCl_2$$

$$3Ca + N_2 \rightarrow Ca_3N_2 \; ; \; Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

16.5. STRONTIUM AND BARIUM

A brief resume of the chemistry of these two elements has been presented in Table 16.2

EXERCISES

1. Present a comparative study of the alkaline earths.
2. Magnesium is a member of group IIA of the periodic table. Yet it has many points of resemblances with lithium of group IA. Enumerate these resemblances and offer an explanation of such behaviour.
3. What are sorel cement and plaster of Paris? What are their uses?
4. Starting from $CaCO_3$ how would you get the following compounds?
   (*a*) CaO (*b*) Ca(OCl)Cl (*c*) $CaSO_4$ (*d*) cement (*e*) glass (*f*) calcium cyanamide (*g*) acetylene
5. Describe the preparations of bleaching powder and superphosphate of lime. Point out their uses.
6. What is Portland cement? How is this manufactured? What is reinforced concrete?
7. Give a comparative study of the chemistry of strontium and barium.
8. How would you proceed to extract magnesium from sea water?

CHAPTER 17

GROUP IIIB : BORON AND ALUMINIUM

17.1. INTRODUCTION

This group of the periodic table consists of the elements boron, aluminium, gallium, indium and thallium. All these elements belong to the family of representative elements i.e either they have no *d* electrons (as in boron and aluminium) or that their *d* orbitals (or *f* orbitals) are electron saturated. All these elements have three electrons (i.e. $s^2 p^1$) in their outer quantum shells. Of these three electrons sometimes the s^2 electrons are inert so that they give rise to two valences + 1 and + 3. This is true of the last three members gallium, indium and thallium. But boron and aluminium show only one valence, namely + 3, as is expected of their positions in the group IIIB. In this elementary text we will briefly deal with the chemistry of boron and aluminium.

17.2. A COMPARATIVE STUDY OF THE CHEMISTRY OF BORON AND ALUMINIUM

Typical of the representative elements both boron and aluminium exhibit only the group valence + 3. Table 17.1 records some of the more important physical properties of these two elements.

Table 17.1. A Comparative Study of Some Properties of Boron and Aluminium

Element	Atomic Number	Electron Configuration	Ionisation Potential	Electronegativity	Ionic Radius (M^{3+}) (A)	Reduction Potential $M^{3+} + 3e \rightleftharpoons M$(volts)	M.P (°C)
Boron	5	$[He]2s^22p^1$	8.29 25.15 37.92	2.0	0.2	—	~2200
Aluminium	13	$[Ne]3s^23p^1$	5.98 18.82 28.44	1.5	0.52	−1.66	660

Physical Properties : 1. Both the elements have three electrons (s^2p^1) over the preceding noble gas electronic core. The electronic configuration justifies their inclusion in group IIIB.

2. Since their electronic configuration shows three electrons outside the noble gas configuration as many as three ionisation potentials have to be considered for the formation of ionic compounds. According to Fajans' rules the

sumtotal ionisation potential being rather high in boron than in aluminium it is likely that boron (III) will mostly give covalent compounds while aluminium (III) is likely to give both ionic and covalent compounds. A study of the properties of their compounds justifies this conclusion.

3. Boron has three electrons on its outer orbitals. Hence through three covalent bonds it can at best get a sextet and will still remain short of the stable noble gas octet. This makes tricovalent boron compounds very good Lewis acids i.e. electron acceptors. The well known compound $H_3N \rightarrow BF_3$ serves as a fine example of the Lewis acid character of tricovalent boron compounds. This property is much less pronounced in aluminium.

4. It is a general rule with representative elements that as we move down a group metallic character increases. This increase in metallic character is reflected in decreasing ionisation potential and increasingly more negative reduction potentials. In keeping with this general trend we find that boron is entirely a nonmetal while aluminium is quite metallic. A spectacular display of this difference is exhibited by the fact that boron is a non-conductor while aluminium is a very fine conductor. It may be pointed out that nowadays for electrical transmission costly copper wires are being replaced by cheaper aluminium wires.

5. As expected electronegativity falls from boron to aluminium.

6. Once again in conformity with general group trends the radius of the trivalent cation increases from boron to aluminium.

Chemical Properties : 1. That base character usually increases down a particular group is revealed in the properties of the oxides of the two elements. While B_2O_3 is entirely acidic Al_2O_3 is amphoteric. The aluminium oxide dissolves in acids to give salts like $AlCl_3$, $Al_2(SO_4)_3$ etc. It reacts with alkalies to give aluminate $NaAlO_2$, $KAlO_2$. In both cases however there is evolution of hydrogen.

2. Boron is electron deficient. As a result its hydride compounds such as B_2H_6, B_4H_{10} etc. assume a very unusual bridge structure, namely three-centred-two-electron bonds. In aluminium hydride $(AlH_3)_n$ a polymeric structure is known to exist.

3. The halides of boron are monomeric and characteristic of comparable covalent molecules their boiling points increase with increasing molecular weights.

4. Aluminium is placed much above hydrogen in the electrochemical series and as a result reacts with acids to generate hydrogen. In contrast boron is a nonmetal and hence cannot liberate hydrogen from acids.

5. Both form coordination complexes. Usually representative elements are less prone to give coordination complexes. However those elements which are not very basic are known to form some complexes. Boron is known to give complexes with catechol, salicylaldehyde etc.

17.3. BORON

17.3.1. Some Compounds of Boron : In recent times boron chemistry has expanded to a considerable extent. However in this elementary text we describe only a few selected classical compounds.

Diborane : In Chapter 14 we have seen that boron is likely to give volatile covalent hydrides. Since it is not as electropositive as the alkalies its hydrides are not expected to be ionic in nature. In its covalent hydrides the formulas are quite complicated because of the electron deficient character of the element. In fact boron forms a very large number of hydride compounds like B_2H_6, B_4H_{10}, B_5H_9 to mention a few. Of these the simplest is the diborane, B_2H_6.

The boron hydrides were originally described by Stock. His method consisted of decomposing magnesium boride Mg_3B_2 in acids and fractionally cooling the evolved gaseous mixture by passing through a number of condensers maintained at different low temperatures. However diborane cannot be prepared this way because it is decomposed by water. The following two methods are used for the isolation of B_2H_6.

(*a*) A dry etheral solution of BF_3 is slowly added to an etheral solution of lithium aluminium hydride :

$$4BF_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

(*b*) Boron trifluoride is reacted with sodium hydride :

$$6NaH + 2BF_3 \xrightarrow{180°C} B_2H_6 + 6NaF$$

Diborane is readily hydrolysed :

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$$

It also reacts with alkali solution :

$$B_2H_6 + 2NaOH \rightarrow 2NaOBH_2 + 2H_2$$

It reacts with chlorine to form boron trichloride :

$$B_2H_6 + 6Cl_2 \rightarrow 2BCl_3 + 6HCl$$

The nature of bonding in B_2H_6 : In this molecule if we wish to put single covalent bonds between all the participating elements there should be seven such bonds. This will require as many as 14 electrons. But we have at our disposal a total of 12 electrons : six coming from the two borons and six coming from the six hydrogens. At one stage it was suggested that there are two one-electron bonds to account for the twelve bonding electrons. But this would mean that the molecule has two unpaired electrons i.e. it should be paramagnetic. ($\mu = \sqrt{n(n+2)}$ $= \sqrt{2(2+2)} = 2.83$ B.M.). However the compound is diamagnetic. This indicates that there is no unpaired electron in the compound. The current accepted picture is the concept of three-centred-two-electron bonds. Each of the borons is assumed to be roughly sp^3 hybridised. Each boron makes usual two electron covalent bonds with two terminal hydrogen atoms. Each boron then overlaps with one of the two remaining sp^3 hybrid orbitals of the other boron through the $1s$ orbital of one bridging hydrogen. Thus there is a three centred B—H—B bond. Here one electron comes from the bridging hydrogen and the second electron comes from one of the two borons. Similarly the second B—H—B bond is formed. Fig 17.1 gives a pictorial representation of the bonding.

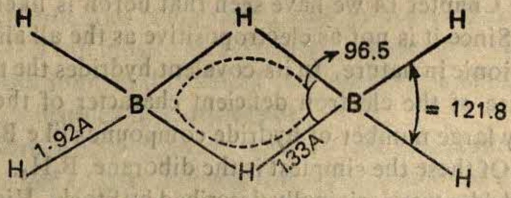


Fig. 17.1. Bonding in diborane, B_2H_6

These three-centred orbitals also follow Pauli exclusion principle i.e. they can accommodate at most two electrons. The bond angles indicate that the hybridisation of boron is not exactly sp^3 as a true sp^3 hybridisation requires a bond angle of 109°. The experimental bond angles for the terminal $<H-B-H$ and the bridging $<H-B-H$ are 121.8 and 96.5°. Out of the six hydrogen atoms only four can be substituted by methyl groups but not the other two. These two hydrogens which resist substitution are the bridging ones. *Such bridge bonds are called hydrogen bridge bonds and are not quite the same as the hydrogen bond. While hydrogen bonds result from an electronegativity difference between the interacting elements hydrogen bridge bonds occur between elements of similar electronegativity and arise out of electron deficiency in the molecule.*

Boric Acid and Boron Trioxide : Boric acid is usually obtained by the reaction of acids on natural borax. The reaction mixture of borax and HCl is boiled, filtered and concentrated to get crystals of boric acid. Acid hydrolysis or simple hydrolysis of boron halides also gives boric acid :

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3$$

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$$

Boric acid has a distinct volatility and is removed on prolonged treatment with hot HCl. The free acid decomposes on heating to boron trioxide according to the following steps :

$$H_3BO_3 \xrightarrow{100°C} HBO_2 \xrightarrow{140°C} H_2B_4O_7 \xrightarrow{>140°C} B_2O_3$$

Free boric acid reacts with alcohol to give boric ester which burns with a green flame :

$$H_3BO_3 + 3CH_3OH \rightarrow B(OCH_3)_3 + 3H_2O$$

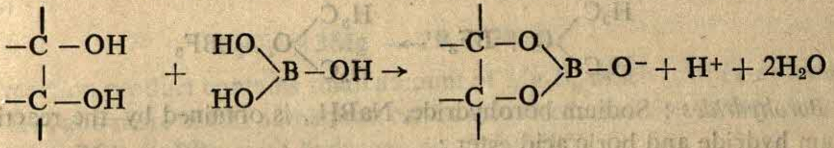
Several transition metal salts react with boric oxide to give characteristically coloured metaborates :

$$CuO + B_2O_3 \rightarrow Cu(BO_2)_2 \quad \text{(blue)}$$

These metaborates form the essence of borax bead tests described in Chapter 28 dealing with qualitative analysis.

Boric acid is a weak tribasic acid, the first acid dissociation constant being 6.0×10^{-10}. Such weak dissociation makes it difficult to determine the amount of boric acid titrimetrically against a standard base. However boric acid is known to form complexes readily with hydroxyl group present in organic compounds like glycerol, mannitol etc. On complexation the hydrogen attached to the –OH groups of H_3BO_3 are easily released so that titration of the released H^+ ion in the presence of a suitable indicator like phenolphthalein becomes possible :

$$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^- \; ; \; K_A^I = 6.0 \times 10^{-10}$$



$$\begin{array}{l} -\overset{|}{C}-OH \\ -\underset{|}{C}-OH \end{array} + \begin{array}{l} HO \\ HO \end{array}\!\!>B-OH \rightarrow \begin{array}{l} -\overset{|}{C}-O \\ -\underset{|}{C}-O \end{array}\!\!>B-O^- + H^+ + 2H_2O$$

Borax: This is sodium tetraborate decahydrate and occurs as a natural source in California. The compound of commerce is usually extracted from this natural source. It is dissolved in water, filtered and then allowed to crystallise. When the temperature is maintained above 60°C the tetraborate crystallises as a pentahydrate and when the temperature is maintained below that temperature the usual decahydrate is obtained. An aqueous solution of borax shows alkaline pH because of hydrolysis :

$$Na_2B_4O_7 + 3H_2O \rightarrow 2NaBO_2 + 2H_3BO_3$$

Borax can also be obtained from the naturally occurring colemanite, $Ca_2B_6O_{11}.5H_2O(= 2CaO.3B_2O_3 + 5H_2O)$. Colemanite is finely powdered and then boiled with a solution of Na_2CO_3. Precipitated $CaCO_3$ is filtered off and the filtrate concentrated to get borax. Some metaborate remaining is converted to borax by reacting with CO_2 :

$$2CaO.3B_2O_3 + 2Na_2CO_3 \rightarrow Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3\downarrow$$

$$4NaBO_2 + CO_2 \rightarrow Na_2B_4O_7 + Na_2CO_3$$

On heating the borax swells, loses the hydrate water and then breaks up into sodium metaborate and boric oxide :

$$Na_2B_4O_7.10H_2O \rightarrow 2NaBO_2 + B_2O_3 + 10H_2O$$

Fused borax (i.e. in fact B_2O_3) reacts with a number of transition metal salts to give metaborates of typical colour :

$$CuO + B_2O_3 \rightarrow Cu(BO_2)_2 \quad \text{(blue)}$$

A few more examples are : $Co(BO_2)_2$, deep blue ; $Cr(BO_2)_3$, green ; $Fe(BO_2)_3$, brown etc. Details of the borax bead tests are given in Chapter 28.

Borax finds use in the making of optical glass, hard glass, enamels, in ceramic industry and in polishing.

Boron Halides : Of these the fluoride and the chloride are more important. These halides are obtained by the following procedures :

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \rightarrow 2BF_3 + 3CaSO_4 + 3H_2O$$

$$2B + 3F_2 \rightarrow 2BF_3 \; ; \; B_2O_3 + 3PCl_5 \rightarrow 2BCl_3 + 3POCl_3$$

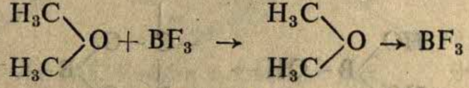
$$B_2O_3 + 3C + 3Cl_2 \rightarrow 2BCl_3 + 3CO$$

These halides are readily hydrolysed to boric acid hydrohaloboric acid.

$$4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3HBF_4$$

On the addition of KCl to this solution KBF_4 crystallises. These halides are good Lewis acids because of their electron deficient character. They readily react with molecules having lone pair of electrons :

$$BF_3 + NH_3 \rightarrow F_3B \leftarrow NH_3$$



$$(H_3C)_2O + BF_3 \rightarrow (H_3C)_2O \rightarrow BF_3$$

Borohydrides : Sodium borohydride, $NaBH_4$, is obtained by the reaction of sodium hydride and boric acid ester :

$$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$$

Lithium borohydride has been obtained by an alternative method of reacting B_2H_6 and LiH :

$$B_2H_6 + 2LiH \rightarrow 2LiBH_4$$

Borohydrides are strong reducing agents. These are often used in organic chemistry in reducing an acid or a keto group to an alcoholic group.

Borazole (*Borazine*): This is a cyclic compound (Fig. 17.2) containing alternate $\rightrightarrows$ BH − and − NH $\rightrightarrows$ groups. This is obtained by the reaction of NH_4Cl and BCl_3 following the given reaction sequence :

$$3NH_4Cl + 3BCl_3 \xrightarrow[140-150°C]{C_6H_5Cl} B_3N_3Cl_3H_3 \xrightarrow[ether]{NaBH_4} B_3N_3H_6$$

This compound is hexagonal planar like the organic benzene. Just as in benzene we conceive of resonating double and single bonds between the the carbon atoms

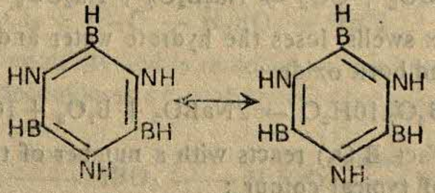


Fig. 17.2 Borazole

so also in borazole. The real structure is a resonance hybrid of the two structures shown in Fig. 17.2. There are a good many similarities in the properties of benzene and borazole. Because of these similarities borazole is nicknamed as *inorganic benzene*. Some properties of benzene and borazole (borazene) are noted below :

	Borazole	Benzene
molecular weight	80.5	78
boiling point (°C)	53	80
heat of vapourisation (KCal/mole)	7	7.4

Borazole is more reactive compared to benzene. Benzene does not undergo addition reaction but borazole does :

$$B_3N_3H_6 + 3HX \rightarrow (-H_2N-BHX-)_3 \quad (X = Cl, OH, OR)$$

17.3.2. Preparation of Boron : Although the element occurs in nature in good quantity as borax ($Na_2B_4O_7.10H_2O$) and colemanite ($Ca_2B_4O_{11}.5H_2O$) it cannot be directly made from these sources. The practical starting point is boric acid H_3BO_3. This is ignited to B_2O_3 which is next reduced by heating with magnesium metal :

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO$$

The reaction product contains small amount of Mg_3B_2 which can be decomposed with HCl and more or less pure boron can be recovered. An alternative procedure is heating BCl_3 or BBr_3 with hydrogen around 1500°C

$$2BCl_3 + 3H_2 \rightarrow 2B + 6HCl$$

Properties : Boron is inactive at ordinary temperature. However at elevated temperatures it reacts with halogens, magnesium etc. to form boron halides, magnesium boride etc. It reacts with oxidising acids :

$$B + 3HNO_3 \rightarrow H_3BO_3 + 3NO_2$$

17.4. ALUMINIUM

17.4.1. Some Compounds of Aluminium : A few selected compounds of aluminium are described below :

Hydroxide and Oxide : Aluminium (III) hydroxide is precipitated on the addition of NH_4OH to a solution of some aluminium salt. This usually separates as a somewhat gelatinous precipitate and is soluble in both acids and bases :

$$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl$$

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

Aluminium oxide is known to form mixed oxide of the spinel type $M^{II}M_2^{III}O_4$ with oxides of bipositive elements :

$$CoO + Al_2O_3 \xrightarrow{\text{heat}} CoAl_2O_4 \text{ (Thenard's blue)}$$

$$MgO + Al_2O_3 \xrightarrow{\text{heat}} MgAl_2O_4$$

$$NiO + Al_2O_3 \xrightarrow{\text{heat}} NiAl_2O_4$$

Aluminium oxide occurs in two major crystalline forms. Alpha alumina occurs in nature as *corundum*. This alpha form is resistant to aqueous acid. Precious stones are mostly corundum containing traces of transition metal oxides : *sapphire* (blue due to cobalt oxide), *ruby* (red due to chromium oxide), *amethyst* (violet due to manganese oxide). Gamma alumina is soft and is easily worked up with acids. Freshly precipitated $Al(OH)_3$, when dried at 400°C, gives *active* gamma alumina. This is voluminous and porous and is ideally suitable for adsorption chromatography. Gamma alumina is transformed into alpha alumina when heated to 1000°C and loses its adsorption capacity.

Alundum is a specially prepared variety of aluminium oxide. Bauxite, $Al_2O_3.2H_2O$, is fused in an electric arc furnace around 3000°C when accompanying materials like silica and other impurities collect below fused bauxite. The whole mass is cooled and the upper part is crushed. The crushed material is then mixed with little felspar, $K_2O.Al_2O_3.6SiO_2$, and clay (or kaolin) $Al_2O_3.2SiO_2.2H_2O$ and is ignited to get alundum. This is extremely heat resistant and finds use in the construction of the interior walls of electric furnaces, Alundum is also used in the making of artificial gems. This is mixed with the requisite amount of the transition metal oxide and is carefully fused in an oxy-hydrogen blow-pipe to get the desired artificial gem.

Aluminium Chloride : This is one of the most important compounds of aluminium. The anhydrous form is in great demand as a catalyst in many important syntheses in organic and organometallic chemistry. The anhydrous form is obtained by two major methods :

(*a*) by passing dry HCl gas over hot aluminium metal and collecting the anhydrous $AlCl_3$ in a cold receiver :

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$

(*b*) by passing dry chlorine gas over aluminium and collecting the anhydrous $AlCl_3$ in a cold receiver :

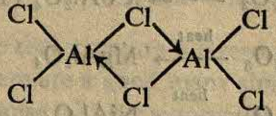
$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

Anhydrous aluminium chloride is extremely sensitive towards moisture and gets hydrolysed :

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$$

Crystals of $AlCl_3.6H_2O$ can be had by dissolving metallic aluminium in dilute HCl and crystallising the solution. So long as the medium is sufficiently acidic hydrolysis will remain suppressed.

Anhydrous aluminium chloride can be readily sublimed. Its vapour density indicates that the compound is dimeric. The two aluminium atoms are bridged by two chlorine atoms. Each aluminium has two terminal chlorine atoms as shown below :



That this is a good covalent compound is shown by its dimerisation, its ready sublimation, its non-electrolytic character and solubility in many organic solvents.

Aluminium Sulphate : This compound crystallises as the 18 hydrate. Bauxite is dissolved in dilute H_2SO_4 and the resulting solution is concentrated and crystallised :

$$\begin{array}{c} Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O \\ \big\downarrow H_2O \\ Al_2(SO_4)_3.18H_2O \end{array}$$

Aluminium Alums: These are double sulphates of aluminium (III) and other chosen monovalent cations crystallising with 12 molecules of water : $M^{I}Al(SO_4)_2.12H_2O$. The common monovalent cations are ammonium, sodium, potassium, rubidium and caesium. The common alum that we purchase from the market is the potassium aluminium alum. These alums are obtained by mixing the monovalent sulphate (eg. K_2SO_4) and the aluminium sulphate ($Al_2(SO_4)_3.18H_2O$) in water in 1 : 1 ratio and then allowing to crystallise.

Potash alum is used in purification of water, as an antiseptic, and in processing of hide. It is used as a *mordant* in dyeing. Cotton fabrics do not easily take a colour on a lasting basis. In order to have a fast colour the cotton fabrics are usually soaked in a solution of potash alum and then treated with dilute NH_4OH. This results in a fine coating of $Al(OH)_3$ on the cotton fabric and thereafter colouring becomes fast.

Lithium Aluminium Hydride : This is prepared by reacting lithium hydride and anhydrous aluminium chloride in etheral solution :

$$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl$$

The lithium chloride is precipitated out while from the filtrate lithium aluminium hydride is recovered. This is a very powerful reducing agent and can reduce an aldehyde or a carboxylic acid group to an alcohol :

$$4CH_3COOH + 3LiAlH_4 \rightarrow LiAl(CH_3CH_2O)_4 + 2LiAlO_2 + 4H_2$$

$$LiAl(CH_3CH_2O)_4 + 4H_2O \rightarrow 4CH_3CH_2OH + LiOH + Al(OH)_3$$

17.4.2. Diagonal Relationship Between Beryllium and Aluminium : We have already come across the pair lithium and magnesium which shows diagonal relationship. An even better pair is beryllium of group IIA and aluminium of group IIIB of the periodic table. Their charge, ionic radii and the charge/radius ratio are given below :

	Beryllium	Aluminium
Charge of the ion	+2	+3
Radius of the ion	0.31	0.51A
Charge/radius	6.4	6.0

The following are the striking similarities in their chemistry :

1. Both the hydroxides are amphoteric in nature. For example in HCl beryllium and aluminium hydroxides give $BeCl_2$ and $AlCl_3$ respectively. In NaOH we get sodium beryllate Na_2BeO_2 and sodium aluminate $NaAlO_2$:

$$Be(OH)_2 + 2NaOH \rightarrow Na_2BeO_2 + 2H_2O$$

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

2. Both the elements have negative reduction potentials : Be, -1.85 Al, -1.66 volts. Thus both liberate hydrogen from acids.

3. In nature both the elements are found to occur together in the mineral beryl : $3BeO.Al_2O_3.6SiO_2$.

4. Both the elements are extracted via electrolysis. Anhydrous $BeCl_2$ is mixed

with NaCl to give a sufficiently conducting mixture. For aluminium Al_2O_3 is dissolved in fused cryolite Na_3AlF_6 and then electrolysis is carried out. The metals as usual are liberated at the cathode.

5. Both the elements do give covalent as well as coordination complexes. Aluminium chloride is a chlorobridged dimer while beryllium chloride is polymeric.

6. The carbides of these two elements belong to the family of methanides. As a consequence they are hydrolysed to give CH_4 :

$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

17.4.3. Industrial Preparation of Aluminium : Aluminium exists in nature in a variety of forms : felspar, $K_2O.Al_2O_3.6SiO_2$; kaolin (clay) $Al_2O_3.2SiO_2.2H_2O$; bauxite, $Al_2O_3.2H_2O$; cryolite, Na_3AlF_6 ; alumstone $K_2SO_4.3Al_2(SO_4)$ $(OH)_4$ etc. In some of these minerals aluminium is very strongly bonded in chains with silicon and oxygen atoms. It has therefore not proved quite viable to extract aluminium from the silicate minerals. Bauxite is, however, the practical ore of aluminium. Very early in the development of the extraction procedure bauxite used to be converted to chloride which was then reduced by metallic sodium. Evidently extraction of aluminium by this technique proved very costly.

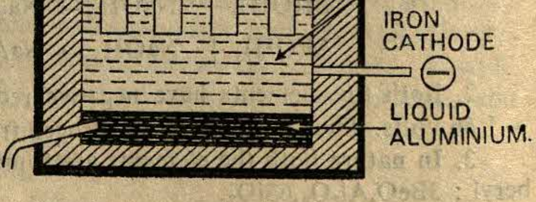
The credit of developing the present cheap method of electrolysis goes to two young men Hall and Heroult. They for the first time discovered that bauxite could be dissolved in molten cryolite and that on electrolysis of this solution aluminium could be obtained at the cathode.

Bauxite contains some impurities like Fe_2O_3 and SiO_2. The impure bauxite is worked up with NaOH solution around 150°C under pressure. Under these conditions Fe_2O_3 remains unaffected while Al_2O_3 and SiO_2 are converted to $NaAlO_2$ and Na_2SiO_3 :

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

The filtered solution is then treated with either (*a*) freshly precipitated Al $(OH)_3$ or (*b*) gaseous CO_2 when $Al_2O_3.xH_2O$ (or $Al(OH)_3$) separates out. The precipitated hydroxide is next heated to get rid of the water and the oxide is then added to fused artificial cryolite Na_3AlF_6 maintained at about 1000°C. The electrolyte is taken in a rectangular iron vessel serving as the cathode. Inside the fused electrolyte are suspended a few



Ftg. 17.3. Extraction of aluminium

carbon rods serving as anode. Aluminium is liberated at the cathode and the liquid metal is drawn out through a hole at the bottom. Oxygen is liberated at the graphite rods. The liberated oxygen attacks the graphite rods and CO_2 and CO are evolved :

at the cathode : $2Al^{3+} + 6e \rightarrow 2Al$

at the anode : $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e$

$$(C + \tfrac{1}{2}O_2 \rightarrow CO \; ; \; C + O_2 \rightarrow CO_2)$$

In some of the latest designs a mixture of fluorides of aluminium, sodium and calcium is used instead of cryolite. This brings down further the temperature of the fused mass. Moreover this solvent has a lower density and hence aluminium settles easily at the bottom of the electrolytic cell.

Young readers should convince themselves why sodium is not liberated at the cathode as also why fluorine is not evolved at the anode. A study of the reduction potentials (Na^+/Na, − 2.71 ; Al^{3+}/Al, − 1.66 volts) reveals that sodium gives up its electron far more readily than aluminium i.e. it is far more difficult to reduce sodium ion than aluminium ion. Similarly the reduction potential of $F_2/2F^-$ (2.65 volts) indicates that it is extremely difficult to oxidise fluoride ion to fluorine gas.

Properties : It is a light, white metal with enough electrical conductivity. We have earlier mentioned that aluminium wires are now being used for transmission of electricity. It is coated with a layer of $Al(OH)_3$ when exposed to an atmosphere of moist air. At elevated temperature the metal is an excellent reducing agent. Goldschmidt's alumino thermite process is based on this property of the metal. We have also mentioned at the beginning that the metal is amphoteric in behaviour :

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

With halogens the metal produces aluminium halides and with nitrogen aluminium nitride.

Uses : Aluminium and its alloys are light and at the same time are quite hard. Because of this, the metal finds a variety of uses in alloys used in the making of utensils, aeroplane parts, as roofing materials, as collapsible tubes for toothpastes, cosmetics, as food packaging materials.

duralumin	: Cu 3.5 − 4.5% ; Mg 0.3 − 1.0% ; Mn 0.4 − 1.0% ; Si 0.3 − 1.0% ; Al 92.5 − 95.5%
aluminium bronze	: Cu 90%, Al ~ 10%
magnelia	: Al 98% ; Mg ~ 2%

17.4.5. Goldschmidt Thermite Process : We have already talked of the basis of this process in Chapter 13. Metallic aluminium is capable of reducing oxides of those metals whose reduction potentials are less negative i.e. more positive than that of aluminium. Thus the reduction potentials of Fe^{3+}/Fe, Cr^{3+}/Cr, Mn^{2+}/Mn etc. are less negative than the reduction potential of Al^{3+}/Al ($-$ 1.66 volts). At elevated temperature the reduced metal is obtained in a fused state. Goldschmidt utilised this method of reduction for welding of broken parts of iron.

The broken parts of iron are placed in position. Above this is held a heat resistant crucible provided with a hole at the bottom. Inside the crucible is taken the thermite — in this particular case a mixture of aluminium powder and ferric oxide. Inside the thermite is introduced the end of a magnesium wire. In order to assist the burning of the magnesium fuse the thermite is covered with a mixture of magnesium powder and barium peroxide. On igniting the magnesium fuse there is explosion inside the thermite mixture. The heat generated helps in the reduction of the ferric oxide by metallic aluminium :

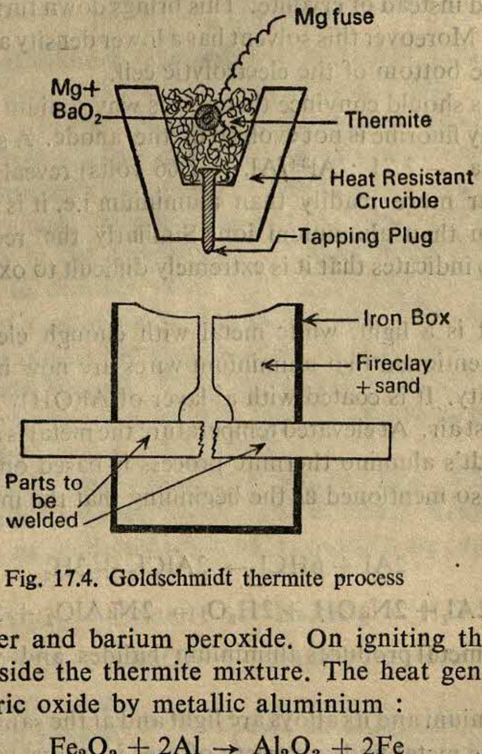


Fig. 17.4. Goldschmidt thermite process

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$$

The molten iron rolls out through the hole of the crucible and drops on the broken parts of iron and does the job of welding the two pieces together.

EXERCISES

1. Make a comparative assessment of the chemistry of boron and aluminium.
2. Does aluminium have any diagonal relationship with beryllium of group IIA of the periodic table?
3. Which of boron and aluminium is likely to show more of metallic properties?
4. How elementary boron can be obtained from borax?
5. Discuss the properties, syntheses and bonding of diborane and borazole.

6. How would you proceed to prepare anhydrous aluminium chloride? What is its structure? Mention its uses.

7. Give a description of Goldschmidt thermit process. Is it possible to use this method for reduction of oxides of those elements whose reduction potentials are more negative than that of aluminium?

8. Describe the extraction of aluminium from natural bauxite. Mention some properties and uses of the element.

9. What are alums and schonites? Describe the synthesis of common alum. Can you grow mixed crystals from a solution of potassium aluminium sulphate and potassium chromium sulphate?

10. Complete the following reactions :

(*a*) $BF_3 + LiAlH_4 \rightarrow$

(*b*) $B_2H_6 + 6H_2O \rightarrow$

(*c*) $CuO + B_2O_3 \rightarrow$

(*d*) $BF_3 + NH_3 \rightarrow$

(*e*) $B_2O_3 + 3CaF_2 + 3H_2SO_4 \rightarrow$

11. Write notes on the following compounds :
(*a*) borax (*b*) borohydrides (*c*) borazole (*d*) aluminium oxides

12. Mention some alloys of aluminium alongwith their uses.

CHAPTER 18

GROUP IVB : CARBON, SILICON, TIN AND LEAD

18.1. INTRODUCTION

This group comprises the five elements : carbon, silicon, germanium, tin and lead. All these elements have four electrons in their outermost quantum shell and hence according to rules they are all members of the fourth group of the periodic table. According to the group position all these elements should show only the group valence four, since they all are representative elements. However there is noticed a variation in valence because of the s^2 inert pair. As in the case of the group IIIB elements valence varies by two units i.e. they show either the group valence four or a valence two. Thus we find carbon, tin and lead form bivalent and quadrivalent compounds.

18.2. A COMPARATIVE STUDY OF CARBON, SILICON, TIN AND LEAD

Physical Properties : 1. Outer quantum shell electron distribution of all the four elements is s^2p^2. There is some difference in the stability of the electrons in these two levels. For this reason we find two different valences in their chemistry : $+2$ and $+4$. The valence changes by two units indicating the inertness of the electron pair. This electron pair is therefore termed *inert pair.*

2. The four outermost electrons will have four ionisation potentials and these *mostly* tend to decrease with increasing atomic number (Table 18.1). This explains why carbon is wholly a nonmetal while tin and lead are metals. Carbon and silicon are covalent in their compounds while tin and lead exhibit ionic or covalent character depending on the valence. Following Fajans' rules in the bivalent state both tin and lead are ionic while in the quadrivalent state they are covalent.

3. Allotropy of carbon is much too well-known (Chapter 10). The other elements also show allotropy to some extent.

Chemical Properties : 1. Following the classification of hydrides (Chapter 14) all these elements give volatile covalent hydrides. Of these the first member carbon forms by far the most astounding series of hydrocarbons of which some have single bonds, some double bonds, some triple bonds (eg. CH_4, C_2H_4, C_2H_2). Carbon forms also long chain aliphatic and aromatic hydrocarbons. As we descend the group the tendency of forming hydrides decreases due certainly to an increase in the metallic character. Silicon does form several hydrides but the stability of SnH_4 and PbH_4 is rather poor.

Table 18.1. A Comparison of some Properties of Group IVB Elements

Elements	Atomic Number	Electron Configuration	Ionisation Potential (*ev*)	Electronegativity	Covalent Radius (A)	Ionic Radius M^{2+}(A)	M.P. (C)
C	6	$[He]2s^22p^2$	11.25 24.38 47.87 64.48	2.50	0.77	—	3500 (diamond)
Si	14	$[Ne]3s^23p^2$	8.15 16.34 33.46 45.13	1.74	1.17	0.39	1400
Sn	50	$[Kr]4d^{10}5s^25p^2$	7.33 14.63 30.60 39.60	1.72	1.40	0.71	232
Pb	82	$[Xe]4f^{14}5d^{10}6s^26p^2$	7.41 15.03 32.00 42.30	1.54	1.54	0.84	327

2. Carbon has two oxides : CO and CO_2. Carbon dioxide is a gaseous acidic oxide. But SiO_2 is polymeric and hence has a very high melting point. SiO_2 reacts both with acids and alkalies. With HF silicon fluoride and water are formed while with alkalies silicates and water are formed. Similarly SnO is also amphoteric. It reacts with acids to form stannous salts and with alkalies to give stannites (eg. Na_2SnO_2). PbO is a basic oxide.

3. All the tetrahalides are covalent. Of these CF_4 is very stable while $SiCl_4$ is readily hydrolysed. The explanation of the ready hydrolysis of $SiCl_4$ is that the coordination number of silicon may reach six and that it has *d* orbitals. The H_2O molecules can readily get attached to the *d* orbitals and can bring about the hydrolysis :

$$SiCl_4 + 2H_2O \xrightarrow{\text{heat}} SiO_2 + 4HCl$$

$SnCl_4$ and $PbCl_4$ behave in a parallel manner.

4. Of the different oxides of this group CO is very important. It readily forms very many carbon monoxide complexes called *carbonyls*. $Ni(CO)_4$ is a very important one which finds use in the preparation of very pure nickel.

18.3. ALLOTROPY

A general discussion of allotropy has already been made in Chapter 10. As we move from carbon to lead there is gradual increase in metallic character. The three major allotropic forms of carbon are diamond, graphite and amorphous carbon. Diamond is the result of formation of giant molecule composed of carbon atoms held through overlap of sp^3 hybrid orbitals of the carbon atoms. In graphite we have a layer structure made up of hexagonal array of carbon atoms. These carbon atoms are planar sp^2 hybridised. The third *p* orbitals of the six carbon atoms of each C_6 unit overlap to give molecular orbitals (for details see Chapter 10). In between the hexagonal planar layers there is a weak van der Waals bond. It is a general observation that with increasing size of the atoms the power to form double or triple bonds decreases. As a consequence we find that in silicon and in tin (below 13°C) there is non-ending diamond like bonding but no such bonding appears in lead presumably because of its increased metallic character. Also to be noted is that there is metallic bonding in tin (above 13°C) and lead but no such bonding occurs in carbon and silicon. Graphite structure is found only in carbon and not in any of the remaining elements.

18.4. CARBON

In Fig. 18.1. is given a representative idea about the syntheses of important carbon compounds starting from carbon.

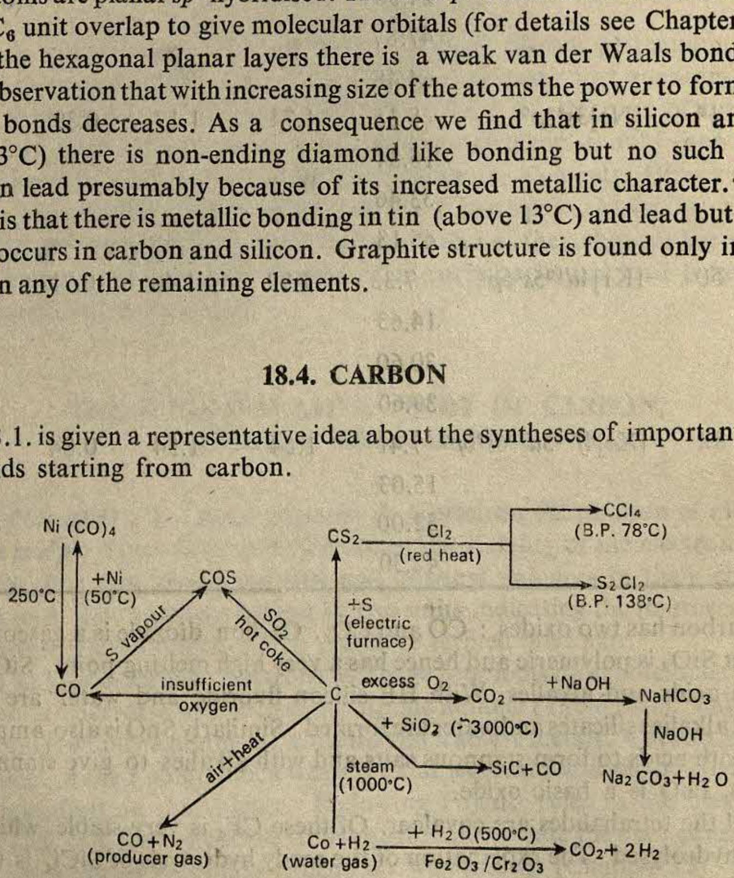


Fig. 18.1. Syntheses of several carbon compounds starting from carbon

18.4.1. Producer Gas and Water Gas : Water gas is formed when heated steam is led over coke maintained at around 1000°C.

$$C + H_2O \xrightarrow{1000°C} H_2 + CO$$

This gas is a source of industrial hydrogen. In order to recover hydrogen from water gas, the gas is reacted with more steam at 500°C in presence of a Fe_2O_3/Cr_2O_3 catalyst. This reaction produces a mixture of $CO_2 + H_2$ ($H_2 + CO +$

$H_2O \rightarrow CO_2 + 2H_2$). The undesired CO_2 is either dissolved out in some alkali solution or passed through water under pressure. CO_2 is not much soluble in water but dissolves appreciably in water under pressure. Both the constituents of water gas, namely CO and H_2 are combustible in presence of oxygen and hence used in industry as a fuel.

The reaction leading to the production of water gas is endothermic :

$$C + H_2O \rightarrow CO + H_2 - 29\text{KCal}$$

As a result after some amount of water gas has been produced the reaction temperature tends to fall. In order to maintain the temperature at the desired level exothermic producer gas is introduced into the system. Producer gas is obtained by passing air over heated coke :

$$C \xrightarrow[>1000°\text{C}]{O_2\ +\ N_2} CO + N_2$$

It is understood that the amount of air needs to be regulated to get producer gas ($CO + N_2$). It is obvious that too much air would give CO_2 instead of CO. Producer gas is used as an industrial fuel because of the following exothermic reaction :

$$2CO + O_2 \rightarrow 2CO_2 + 136\ \text{KCal}$$

A comparative evaluation of the exothermicity of the two (fuel) gases shows that water gas liberates more heat than producer gas. Exothermicity is usually expressed in BTU (British Thermal Unit). The amount of heat required to raise the temperature of one pound of water through 1°F is called 1 BTU. On this unit the calorific value of one cubic foot of producer gas is 150 BTU while that of water gas is 300 BTU.

18.4.2. Destructive Distillation of Coal : Coal Gas : Destructive distillation of coal means heating coal in a large vertical retort in the absence of air. The retort is made of many chambers. Coal is taken in these chambers. The heating gas namely producer gas and air is introduced through the side inlet near the bottom while coal is pushed in from the top of the retort through a gas tight hopper. The process is continuous. The chambers are made of fireclay bricks and the temperature inside the retort is around 1000°C. Depending on the nature of the coal a variety of products is obtained :

1. Volatile gaseous products like H_2, CH_4, C_2H_4, CO, H_2S etc. These are taken out through an outlet near the top of the furnace.

2. Substances which condense to liquids on cooling. Among these are ammonia, ammonium sulphide, ammonium thiocyanate, ammonium carbonate, pyridine etc.

3. A tarry mass containing a series of aromatic hydrocarbons : C_6H_6, CH_3. C_6H_5(toluene), $C_{10}H_8$ (naphthalene), $C_{14}H_{10}$ (anthracene) C_6H_5OH (phenol) etc.

4. Non-volatile coke

The less volatile tarry matter is taken out through a bigger outlet and is cooled down to around 60°C. The ammonium salts and the tar are separated here. The tar settles down while the other volatile products are led through different condensers. Such manipulation allows separation of the ammonium salts and other aromatic products like benzene and naphthalene.

The volatile gases which are led out through an exit tube near the top of the retort are first washed by passing through a series of water tanks. Any water soluble gas dissolves out. The H_2S is decomposed by reacting the gas with Fe_2O_3 :

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$$

In an alternative procedure the above gas is treated with ethylamine in a scrubber. H_2S is then absorbed as ethylammonium sulphide. The issuing gas is generally referred to as *coal-gas*. Sometimes coal-gas is mixed with water-gas. This mixing, however, does not change the calorific value of coal-gas to any appreciable extent.

18.4.3. Carbon Dioxide : This compound can be obtained in a variety of ways : (a) decomposition of a metal carbonate or a bicarbonate by acids : $CaCO_3 + 2HCl \rightarrow CO_2 + CaCl_2 + H_2O$; (b) thermal decomposition of a metal carbonate : $CaCO_3 \rightleftharpoons CaO + CO_2$; (c) conversion of water gas $(CO + H_2)$ to $CO_2 + H_2$ in presence of steam and a Fe_2O_3/Cr_2O_3 catalyst and removal of the CO_2 by water under pressure.

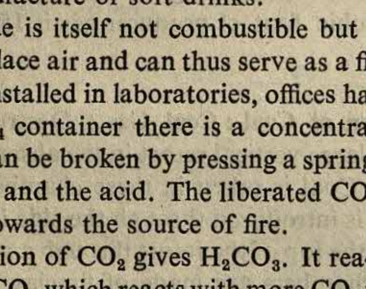
At ordinary temperature and pressure CO_2 is gaseous. It can be liquefied under pressure or by strong cooling. If the liquid CO_2 from a cylinder is allowed to escape through a bag of cloth its rapid and sudden evaporation gives frozen white carbon dioxide popularly called *dry ice*.

Increased pressure makes CO_2 more soluble in water. This property is made use of in the manufacture of soft drinks.

Carbon dioxide is itself not combustible but by virtue of its being heavier than air it can displace air and can thus serve as a fire extinguisher. The ordinary fire extinguishers installed in laboratories, offices have H_2SO_4 in a glass container. Around the H_2SO_4 container there is a concentrated solution of Na_2CO_3. The H_2SO_4 container can be broken by pressing a spring. This results in mixing of the carbonate solution and the acid. The liberated CO_2 is allowed to escape through an exit and held towards the source of fire.

Aqueous solution of CO_2 gives H_2CO_3. It reacts with $Ca(OH)_2$ to form first a precipitate of $CaCO_3$ which reacts with more CO_2 to give the soluble $Ca(HCO_3)_2$. CO_2 finds use as a fire extinguisher, in soda-water, other soft drinks. Dry ice finds good use in the laboratory for low temperature synthetic work.

Structure of CO_2 : It is a linear molecule with a zero dipole moment. On either side of the carbon there are two oxygen atoms bound by double bonds. Carbon is assumed to be *sp* hybridised so that its other two *p* orbitals remain outside the range of hybridisation :



The two unpaired electrons in the two *sp* hybrid orbitals of carbon overlap with two unpaired electrons of the two oxygens. Thus on either side of carbon we have a sigma bond. One *p* electron of carbon (say the p_y) overlaps with a corresponding *p* electron of one oxygen. The remaining *p* orbital (say the p_z) overlaps with the corresponding *p* orbital of the second oxygen. Thus we write the structure of the molecule of CO_2 as given below :

$$O = C = O$$

The two π bonds being along the *y* and *z* axes are at 90° to each other.

18.4.4. Carbon Monoxide : Laboratory method of preparation consists of adding formic acid dropwise into hot (100°C) H_2SO_4. The concentrated H_2SO_4 assists in the removal of the liberated water.

$$HCOOH \rightarrow CO + H_2O$$

The most famous reactions of this compound are the formations of carbonyl complexes of many metals mostly in zero or in negative oxidation state. Some examples are $Ni(CO)_4$, $Fe\ (CO)_5$, $Cr(CO)_6$ etc. Of these compounds nickel tetracarbonyl is of enormous industrial importance. Its formation occurs at ordinary pressure and at around 50°C but the tetracarbonyl breaks down into pure nickel and CO at around 200°C :

$$Ni + 4CO \underset{200°C}{\overset{50°\,C}{\rightleftharpoons}} Ni(CO)_4$$

Carbon being bivalent, this compound behaves as a strong reducing agent

$$PbO + CO \rightarrow Pb + CO_2 \quad ; \quad CuO + CO \rightarrow Cu + CO_2$$

Structure of CO : This is a diatomic molecule and the two interacting partners differ widely in their electronegativities. Effectively there is a triple bond in the molecule. All these make the molecule polar. Both the atoms are assumed to be *sp* hybridised :

$$\begin{array}{lcccc} C & \underset{2(sp)}{\underline{\uparrow\downarrow}} & \underset{2(sp)}{\underline{\uparrow}} & \underset{2p}{\underline{\uparrow}} & 2p \\ O & \underset{2(sp)}{\underline{\uparrow\downarrow}} & \underset{2(sp)}{\underline{\uparrow}} & \underset{2p}{\underline{\uparrow}} & \underset{2p}{\underline{\uparrow\downarrow}} \end{array}$$

Both the atoms have a pair of electrons in one of the two hybrid orbitals. This functions as the lone pair. The lone pair on carbon is donated to the metals in the formation of carbonyls. The lone pair on the oxygen remains unused as it has a higher electronegativity. The two *sp* hybrids — one of carbon and another of oxygen—with an unpaired electron on each overlap to form the sigma bond. The pure atomic *p* orbitals with one unpaired electron on each makes the first pi-bond. The second pi-bond is formed by the overlap of the electron pair in the third p orbital of oxygen with the third empty p orbital of carbon. Thus the triple bond between carbon and oxygen is constituted of one sigma and two pi bonds :

$$\underset{\cdot\cdot}{C} \overset{\leftarrow}{=} \underset{\cdot\cdot}{O}$$

18.4.5. Carbonate and Bicarbonate : Depending on the amount of CO_2 alkalies react to give either a carbonate or a bicarbonate. Carbonates are formed when alkalies are in excess while the bicarbonates are formed when CO_2 is in excess. The group IA alkali metals alone can give the bicarbonates in the solid crystalline state. Even the alkaline earths bicarbonates cannot be obtained in the solid crystalline state. They exist only in solution. Neutralisation of a standard solution of Na_2CO_3 involves interesting chemistry. The neutralisation proceeds in two steps. The first step involves formation of $NaHCO_3$ when the pH of the solution is around 8.7 where phenolphthalein can be used to detect the endpoint (from pink to colourless). The second step involves the formation of H_2CO_3 and a salt like (say) NaCl. The pH at this step is around 4.0 and methyl orange or methyl red can be used for the detection of the end point. The titre value in the first case is just half of that in the second case. For details see Chapter 8.

All carbonates other than those of the alkalies are insoluble in water.

18.4.6. Carbon Disulphide : This is obtained by the interaction of coke and sulphur vapour. The reaction is carried out in an electric furnace. Coke is introduced through the top of the furnace while through a side inlet near the bottom is introduced powdered sulphur. An arc is set between two carbon electrodes fixed into the lower part of the furnace. As the sulphur vapour moves up it reacts with the coke and forms CS_2 which is led out of the furnace through an exit in the upper portion of the furnace. The CS_2 is condensed in coolers to the liquid state.

It reacts with chlorine to form CCl_4 and S_2Cl_2 (18.4.7) :

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

The S_2Cl_2 (disulphur dichloride) reacts with fresh CS_2 in the presence of FeS catalyst to generate more CCl_4 :

$$2S_2Cl_2 + CS_2 \rightarrow CCl_4 + 6S$$

It is used as a solvent in the laboratory. It finds use in rayon industry, in vulcanization of rubber and in the manufacture of CCl_4.

18.4.7. Carbon Tetrachloride : This is made by the action of chlorine on CS_2 in the presence of aluminium chloride or iodine as a catalyst.

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

The two products are separated by making use of the difference in their boiling points : CCl_4, 78°C and S_2Cl_2, 138°C. The reaction products are first condensed to the liquid state and then fractionally distilled. CCl_4 having a lower boiling point will distill out first while sulphur monochloride will require a higher temperature. It is used as a fire extinguisher, as a solvent and in cleaning clothings.

18.4.8. Potassium Cyanide and Hydrocyanic Acid : Preparation of KCN has already been described in Chapter 15. HCN is liberated on treating KCN with acids :

$$K_2CO_3 + C + 2NH_3 \rightarrow 2KCN + 3H_2O$$

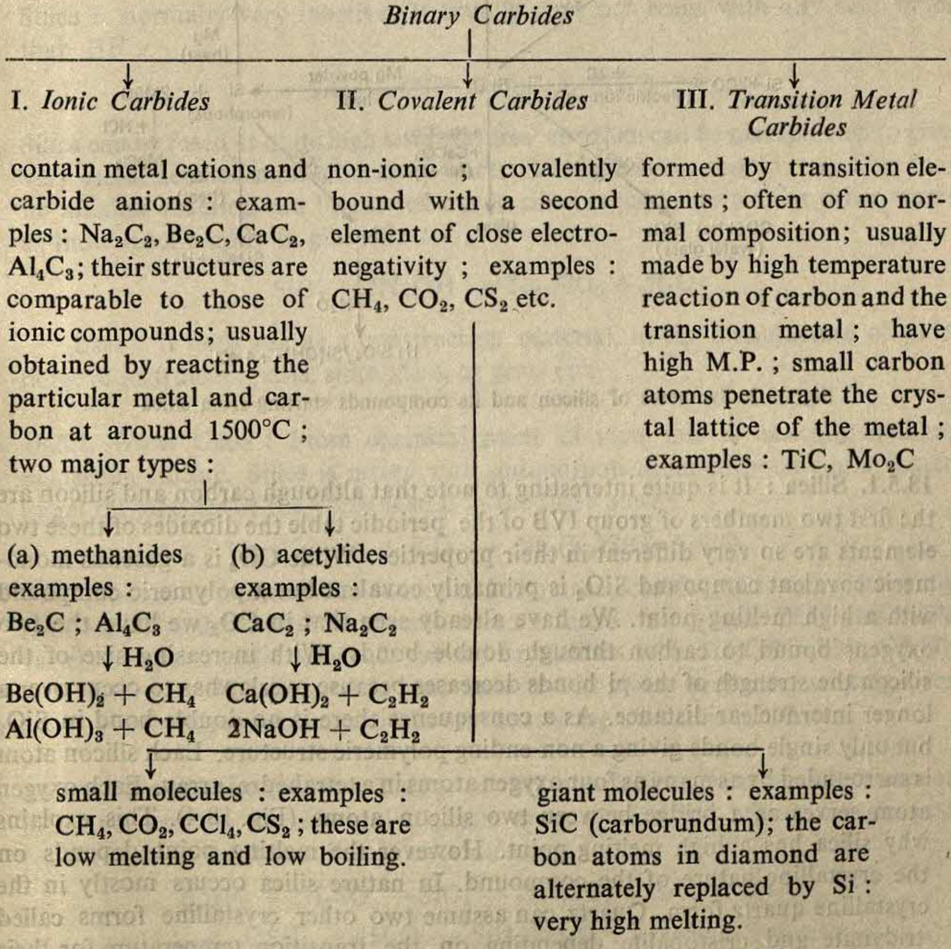
$$KCN + H_2SO_4 \rightarrow KHSO_4 + HCN$$

All metal cyanides will react with acids to give HCN :

$$Hg(CN)_2 + H_2S \rightarrow HgS + 2HCN$$

KCN and HCN are dangerously poisonous. Haemoglobin of blood is the oxygen carrier. It forms a weak complex with O_2 molecule and is converted into oxyhaemoglobin. Cyanide ion is a very strong complexing ligand. As a result on inhaling HCN gas or taking solution of cyanide, the cyanide ion immediately displaces the O_2 molecule and stops the oxygen carrying ability of haemoglobin. The result is paralysis or death.

18.4.9. Binary Carbides : These are compounds of carbon with one other element. Depending on the nature of the bonding and the consequent properties these carbides have been broadly classified into three groups : (a) ionic carbides (b) covalent carbides and (c) transition metal carbides. In Fig. 18.2 is given a concise account of the classification, syntheses and properties of these carbides.



Binary Carbides

I. *Ionic Carbides*

contain metal cations and carbide anions : examples : Na_2C_2, Be_2C, CaC_2, Al_4C_3; their structures are comparable to those of ionic compounds; usually obtained by reacting the particular metal and carbon at around 1500°C ; two major types :

(a) methanides examples : Be_2C ; Al_4C_3 $\downarrow H_2O$ $Be(OH)_2 + CH_4$ $Al(OH)_3 + CH_4$

(b) acetylides examples : CaC_2 ; Na_2C_2 $\downarrow H_2O$ $Ca(OH)_2 + C_2H_2$ $2NaOH + C_2H_2$

II. *Covalent Carbides*

non-ionic ; covalently bound with a second element of close electronegativity ; examples : CH_4, CO_2, CS_2 etc.

small molecules : examples : CH_4, CO_2, CCl_4, CS_2 ; these are low melting and low boiling.

giant molecules : examples : SiC (carborundum); the carbon atoms in diamond are alternately replaced by Si : very high melting.

III. *Transition Metal Carbides*

formed by transition elements ; often of no normal composition; usually made by high temperature reaction of carbon and the transition metal ; have high M.P. ; small carbon atoms penetrate the crystal lattice of the metal ; examples : TiC, Mo_2C

Fig. 18.2. Classification, syntheses and properties of binary carbides

18.5 SILICON

Elementary silicon may be obtained in two allotropic forms. Amorphous silicon is obtained by heating ordinary sand (SiO_2) with magnesium. The MgO, that is formed, is dissolved out by treating the reaction product with hydrochloric acid. The residue left is the amorphous silicon. When SiO_2 is heated with coke in an electric furnace crystalline variety of silicon is obtained.

A variety of silicon compounds and their mode of syntheses are shown in Fig, 18.3.

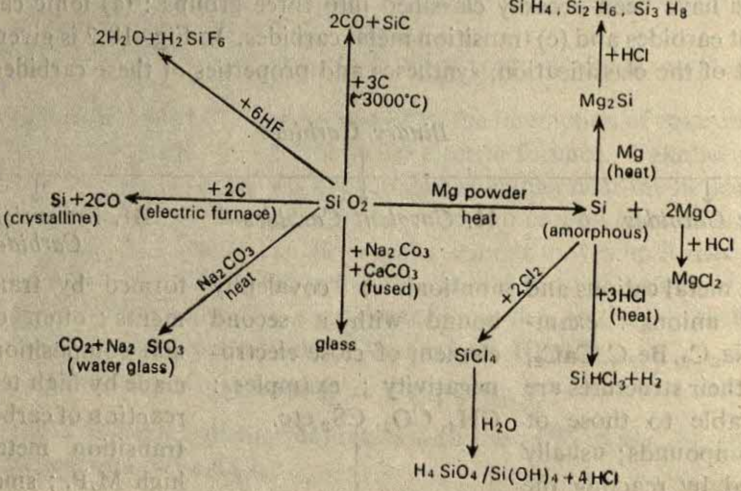


Fig. 18.3. Syntheses of silicon and its compounds starting from silica

18.5.1. Silica : It is quite interesting to note that although carbon and silicon are the first two members of group IVB of the periodic table the dioxides of these two elements are so very different in their properties. While CO_2 is a gaseous monomeric covalent compound SiO_2 is primarily covalent but a polymeric compound with a high melting point. We have already seen that in CO_2 we have the two oxygens bound to carbon through double bonds. With increasing size of the silicon the strength of the pi bonds decreases because overlap has to occur over a longer internuclear distance. As a consequence there is no double bond in SiO_2 but only single bonds giving a non-ending polymeric structure. Each silicon atom is surrounded by as many as four oxygen atoms in a tetrahedral array. Each oxygen atom serves as a bridge between two silicon atoms (Fig. 18.4). This explains why silica has a high melting point. However the melting point depends on the crystalline nature of the compound. In nature silica occurs mostly in the crystalline quartz form. Quartz can assume two other crystalline forms called tridymite and cristobalite depending on the transition temperature for their interconversion,

$$\text{quartz} \overset{870^\circ C}{\rightleftharpoons} \text{tridymite} \overset{1470^\circ C}{\rightleftharpoons} \text{cristobalite}$$

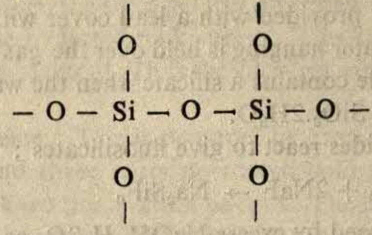


Fig. 18.4. The nature of bonding in silica

In the laboratory we can prepare pure silica by reacting a silicate by acids :

$$(Ca/Na_2)SiO_3 + 2HCl \rightarrow (CaCl_2/2NaCl) + SiO_2 + H_2O$$

Silica is normally very inactive. It usually does not react with any acid other than HF :

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Silica can be fused at quite high temperatures and then can be manipulated to give very useful heat resistant laboratory wares. Young readers should remember that no alkaline reaction can be carried out in silica crucibles or similar other wares as these react readily to give silicates :

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

Uses : It finds use as a construction material, in the manufacture of wide range of instrument parts, silica glass, as gems etc.

18.5.2. Water Glass : From chemical point of view this is basically sodium/potassium silicate. Silica is mixed with sodium/potassium carbonate and heated to get the silicates of the alkali metals in the fused state :

$$Na_2(K_2)CO_3 + SiO_2 \rightarrow Na_2(K_2)SiO_3 + CO_2$$

The product is heated with water and from the soluble part water is partly removed. The thick product thus obtained is called water glass. This is a soluble variety of glass. Sodium silicate usually crystallises with $5H_2O(Na_2SiO_3.5H_2O)$.

Water glass has demand in soap industry, in giving protective coating over wood, in making non-porous bricks and in making dust resistant floors.

18.5.3. Silicon Tetrafluoride : This is readily obtained on heating a mixture of fine sand, calcium fluoride and requisite amount of H_2SO_4. Since the gas gets readily hydrolysed it is collected over mercury.

$$2CaF_2 + 2H_2SO_4 + SiO_2 \rightarrow 2CaSO_4 + SiF_4 + 2H_2O$$

$$3SiF_4 + 4H_2O \rightarrow SiO_2.2H_2O + 2H_2SiF_6$$

The $SiO_2.2H_2O$ appears as a gelatinous precipitate. H_2SiF_6 is also formed. This reaction is made use of in the qualitative detection of silicate ion. The silicate material is mixed with CaF_2 and H_2SO_4 in a lead crucible and is *warmed* on an asbestos board. The crucible is provided with a lead cover with a small hole. A platinum loop with a drop of water hanging is held over the gas coming out of the crucible. If the unknown sample contains a silicate then the water drop will turn turbid due to the formation of $SiO_2.2H_2O$.

SiF_4 and alkali metal fluorides react to give fluosilicates :

$$SiF_4 + 2NaF \rightarrow Na_2SiF_6$$

The fluosilicate is decomposed by excess NaOH, H_2SO_4 as also by heat :

$$Na_2SiF_6 + 4NaOH \rightarrow 6NaF + SiO_2 + 2H_2O$$

$$Na_2SiF_6 + H_2SO_4 \rightarrow Na_2SO_4 + SiF_4 + 2HF$$

$$Na_2SiF_6 \rightarrow 2NaF + SiF_4$$

18.5.4. Silicon Tetrachloride : This is obtained on heating silicon or magnesium silicide with chlorine gas :

$$Si + 2Cl_2 \rightarrow SiCl_4 \ ; \ Mg_2Si + 4Cl_2 \rightarrow SiCl_4 + 2MgCl_2$$

This compound is also readily hydrolysed :

$$SiCl_4 + 3H_2O \rightarrow H_2SiO_3 + 4HCl$$

$SiCl_4$ is reduced by potassium metal :

$$4K + SiCl_4 \rightarrow Si + 4KCl$$

It produces dense white fumes with ammonia.

18.5.5. Silicon Chloroform : This is silicon analogue of chloroform. This is formed when HCl gas is led over heated silicon :

$$Si + 3HCl \rightarrow SiHCl_3 + H_2 \ ; \ Si + 4HCl \rightarrow SiCl_4 + 2H_2$$

The evolved gaseous mixture is condensed when $SiHCl_3$ and $SiCl_4$ are transformed to the liquid state. This liquid is then fractionally distilled to separate the two constituents (B.P : $SiHCl_3$, ~ 32°C; $SiCl_4$, ~ 57°C). It is obvious that $SiHCl_3$ will distill out first. It is readily inflammable. It burns in air with a green flame alongwith white fumes of fine silica :

$$4SiHCl_3 + 2O_2 \rightarrow SiO_2 + 2H_2O + 3SiCl_4$$

It undergoes thermal decomposition at around 800°C :

$$4SiHCl_3 \rightarrow Si + 2H_2 + 3SiCl_4$$

18.5.6. Silica Gel : On the addition of HCl to a solution of sodium silicate a precipitate of silicon dioxide appears in the colloidal form. This precipitate takes the form of a translucent jelly. On heating the water is lost and the material left is called *silica gel.* It has a great tendency of absorbing water. Because of this property silica gel is used as a dehydrating agent in the laboratories. For commercial purpose the anhydrous silica gel is mixed with small amount of blue anhydrous cobalt chloride. When the silica gel has absorbed enough water the cobalt chloride also changes to the hydrated pink variety. This can be again heated to regenerate the blue anhydrous material. Thus the silica gel can be used over and over again.

18.5.7. Carboruduum : This is prepared by heating to about 3000°C a mixture of five parts silica and three parts powdered coke alongwith some saw dust. The saw dust helps to keep the mixture porous. The heating is done in an electric arc furnace—the arc being set between two carbon electrodes. Carbon monoxide burns out at the top of the furnace :

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

After the reaction is over the carborundum is washed first with H_2SO_4 and then with NaOH.

The structure of SiC is parallel to that of diamond. We get the SiC structure on substituting every alternate carbon atom of diamond by a silicon atom. A giant molecule is thus obtained with a tetrahedral arry of —C—Si—C—Si—. Thus in the compound each carbon is surrounded tetrahedrally by four silicon atoms and vice versa. Because of this giant molecule formation carborundum is as hard as diamond and decomposes only at a high temperature (~2200°C).

18.5.8. Glass : Glass is a supercooled liquid which ultimately gets hard. It has no fixed melting point. On raising the temperature it gradually turns into a viscous liquid. Like other chemical compounds it has no definite composition. Ordinary glass is composed of mainly sodium silicate, calcium silicate and enough silica. However there may occur a wide variation in the composition depending on the properties that we expect of the glass. Usually the household glass that is used in windows, doors etc. is a composite of 70% silica, calcium oxide 15% and sodium monoxide (15%). Ordinary glass tubes or rods used in the laboratory also have a similar composition. Heat resistant glass like Pyrex or Hysil contains more silica, 15% boric oxide but much smaller amount of sodium oxide. The very special Jena glass contains some Al_2O_3, B_2O_3 and also ZnO. If the silica or the other added constituents contain any coloured metal oxide then the glass also develops that colour. Sometimes some transition metal oxides are deliberately added to develop a special colour effect.

Glass making furnaces consist of two chambers made of fire resistant bricks. Each chamber can hold a charge of raw material sufficient to produce about 1000 tons of liquid glass. The heating of the chambers is done by a regenerative system of heating. The fuel is a mixture of producer gas ($CO + N_2$) and air. The basic materials of glass are taken in one chamber and the mixture is heated to a temperature of about 1400°C by firing producer gas and air. The spent but still hot gas is led out through the other chamber so that this second chamber also remains preheated. A second charge of the raw materials is now taken in the second chamber and the fuel gas is forced through the second chamber and the spent gas is drawn out through the first chamber. Such alternate heating of the two chambers results in fuel economy.

The raw materials for the preparation of glass are silica (SiO_2 normally free from Fe_2O_3), sodium/potassium carbonate and limestone ($CaCO_3$). At the high temperature of the furnace these materials react to produce different silicates:

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

Sometimes some oxidants like KNO_3 or MnO_2 is added in small amounts alongwith the charge to destroy any undesirable colour that might otherwise appear in the glass.

The liquid glass that flows out of the reaction chamber has to be cooled slowly otherwise the glass becomes brittle. The glass is cooled very slowly so that both the inside and the outside surfaces remain at the same temperature. Such uniform rate of cooling increases the strength of the glass against sudden brittleness. The process of slowly cooling down molten glass to room temperature is known as *annealing*.

18.5.9. Silicates : We have already observed that in silica there exists no discrete single molecules — instead giant molecules exist via the bridging oxygen in between silicon atoms. In nature there are a host of very many different silicates. These are often extremely complicated in structural patterns. In this elementary text we record only a few rather simpler types :

(a) SiO_4^{4-} : orthosilicate ; example Mg_2SiO_4. The basic unit is tetrahedral and monomeric.

(b) $Si_2O_7^{6-}$: two tetrahedral SiO_4^{4-} are linked through a common oxygen atom. One example is thortvitite $Sc_2Si_2O_7$.

(c) $Si_3O_9^{6-}$: three SiO_4^{4-} tetrahedra are linked through three common oxygen bridges. A common example is benitoite $BaTiSi_3O_9$.

(d) $Si_6O_{18}^{12-}$: Six SiO_4^{4-} tetrahedra are linked with each other through the six bridging oxygen atoms. A common example is beryl $Be_3Al_2Si_6O_{18}$.

We have already come across some very useful natural zeolites like $NaAlSiO_4$, $NaAlSi_2O_6$, $NaAlSi_3O_8$. These are also complicated silicates which have ion-exchange properties. These find use as water softening materials (Chapter 14). Another useful silicate material is *ultramarine blue*. This is prepared by fusing together sodium carbonate, kaolin, wood charcoal and sulphur in the presence of air. Its composition and structure are not yet known with certainty. However an approximate formulation is written as $Na_8Al_6Si_6O_{24}S_2$. This finds use in washing of clothes, in whitewashing of houses etc.

18.6. DIAGONAL RELATIONSHIP BETWEEN BORON AND SILICON

Boron and silicon belong to two different groups of the periodic table. Yet there are several similarities in the chemistry of the two elements.

	Boron	Silicon
Charge	+3	+4
Ionic Radius (A)	0.2	0.39
Charge/Radius	15	10

1. Boric acid, H_3BO_3 and orthosilicic acid, H_4SiO_4, react with alcohol to produce alkyl borates, $B(OR)_3$, and alkyl silicate, $Si(OR)_4$, respectively.

2. The hydrides of both the elements are readily hydrolysed to give boric acid and silicic acids respectively.

3. Both the elements produce covalent, volatile hydrides. A few examples are : B_2H_6, B_4H_{10}, SiH_4, Si_2H_6 etc.

4. Oxides of these elements, namely B_2O_3 and SiO_2 are acidic in nature. They react with bases to give metal borates and metal silicates.

5. The acids are weak in both the cases : K_A', H_3BO_3, $\sim 6\times10,^{10}$; K_A', H_4SiO_4, $\sim 10^{-10}$.

18.7. A COMPARATIVE STUDY OF TIN AND LEAD

The outer quantum shell electron distribution of these elements are $5s^25p^2$ and $6s^26p^2$ for tin and lead respectively. Thus they have been included in group IVB of the periodic table. When all the four electrons participate in chemical reactions they give quadrivalent compounds. Sometimes two of these four electrons, namely the slightly lower energy s^2 electrons, remain outside the range of valence electrons so that the elements become bivalent. In these circumstances the s^2 electrons are known to form an inert pair of electrons.

As we have observed in Chapter 5, the lower valent compounds of an element are ionic while higher valent ones are covalent. This is also true for tin and lead. Thus $SnCl_4$ and $PbCl_4$ are definitely covalent (low boiling and non-electrolytic) while $SnCl_2$ and $PbCl_2$ (comparatively higher boiling and electrolytic) are definitely ionic.

Higher valent compounds, as expected, act as oxidants while the lower valent ones are reductants. The reduction potentials of the couples Sn^{4+}/Sn^{2+} and Pb^{4+}/Pb^{2+} are $+0.15$ and $+1.8$ volts respectively. We can easily appreciate that quadrivalent lead is a far more effective oxidant than quadrivalent tin. On the other hand bivalent tin is a far superior reductant than bivalent lead. In practice we see that bivalent tin can easily reduce ferric to ferrous while bivalent lead is ineffective. Again PbO_2 is good enough an oxidant to bring about the oxidation of manganese (II) to permanganate which cannot be effected by SnO_2.

It is a general rule that as we go down a group basic properties increase with increasing atomic number. Both tin and lead in group IVB show metallic properties. The bivalent compounds are electrical conductors. As expected the density of the metals increases from tin (7.3) to lead (11.4).

Both these elements are found as constituents of many alloys :

Bronze : copper ~ 90% ; tin ~ 8%
Solder : lead ~ 50% ; tin ~ 50%
Type metal : lead ~ 80% ; antimony ~ 15% ; tin ~ 3%

18.8. TIN

18.8.1. Some Compounds of Tin : Some selected compounds of tin are described below :

Stannous Oxide and Stannic Oxide : Stannous oxide is precipitated on the addition of an alkali to a solution of a stannous salt. In excess alkali the oxide (or the hydroxide) dissolves to form stannite ion :

$$Sn(OH)_2 + OH^- \rightarrow HSnO_2^- + H_2O$$

Stannite ion is a powerful reducing agent. It reduces permanganate to manganese dioxide and trivalent bismuth to finely divided black metallic bismuth :

$$2KMnO_4 + 3Na_2SnO_2 + H_2O \rightarrow 2MnO_2 + 3Na_2SnO_3 + 2KOH$$

$$2BiCl_3 + 6NaOH + 3Na_2SnO_2 \rightarrow 2Bi + 3Na_2SnO_3 + 6NaCl + 3H_2O$$

Metallic tin is oxidised to the metastannic acid (also known as β-stannic acid) on treatment with nitric acid. On ignition of this acid we get tin dioxide :

$$\begin{array}{l} Sn + 4HNO_3 + (x-2)H_2O \rightarrow SnO_2.xH_2O + 4NO_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{heat} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad SnO_2 \end{array}$$

SnO_2 is insoluble in acids but dissolves in alkalies :

$$SnO_2 + 2KOH \rightarrow K_2SnO_3 \xrightarrow{H_2O} K_2SnO_3.3H_2O$$

On acidification of alkaline K_2SnO_3 a precipitate of α-stannic acid is obtained. α - and β - stannic acids have the same crystal structure but they differ only in their particle size.

Stannous Chloride : Tin is positioned above hydrogen in the electrochemical series. As a result on acidification we get evolution of hydrogen and $SnCl_2$. The salt crystallises with two molecules of water : $SnCl_2.2H_2O$. Anhydrous $SnCl_2$ may be obtained by reacting tin metal with dry HCl gas. In the laboratory stannous chloride solution is preserved over a few pieces of metallic tin in order to suppress oxidation. $SnCl_2$ can reduce ferric to ferrous, mercuric to mercurous and cupric to cuprous state :

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

$$SnCl_2 + 2HgCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$$

Stannic Chloride : This is obtained on oxidation of tin metal with dry gaseous chlorine. It is a colourless liquid. It readily suffers hydrolysis because of nucleophilic attack by H_2O molecules on its empty *d* orbitals.

$$SnCl_4 + 4H_2O \rightarrow 4HCl + Sn(OH)_4$$

Mosaic Gold : A yellow precipitate of SnS_2 is obtained on the passage of H_2S through a solution of $SnCl_4$ in dilute HCl. On commercial scale the compound is obtained by heating a mixture of metallic tin, powdered sulphur and ammonium chloride. The bright golden coloured SnS_2, so produced, is known as *mosaic gold*. It is used as a golden coloured pigment in beautifying porcelain or glass wares.

18.8.2. Industrial Preparation of Tin : In nature tin is found to occur as tinstone or cassiterite. These contain SnO_2, arsenical pyrites (FeAsS), iron pyrites (FeS), silicate etc. Small amounts of wolframite (iron/manganese tungstate: $FeWO_4$/$MnWO_4$) are also often found. The ore is finely ground and then treated with a current of water on a shaking table. Such treatment carries away the lighter silicates alongwith the current of water. But the other heavy impurities like iron pyrites and wolframite are retained with the cassiterite. These impurities are magnetic in nature and are separated from the non-magnetic cassiterite by the application of a magnetic field (Chapter 13). Wolframite and iron pyrites collect close to the magnetic field while the cassiterite collect at some distance away from the magnetic field.

The cassiterite, now contaminated by arsenical pyrites, is burnt in a current of air. Sulphur and arsenic are removed in the form of their volatile oxides. The remaining tin dioxide is mixed with anthracite coal, lime and fluorspar (CaF_2) and is fused around 1200°C :

$$SnO_2 + 2C \xrightarrow{1200°C} Sn + 2CO$$

Fused tin and the slag collect at the bottom of the furnace and are taken out through two holes. The slag contains a good amount of tin. The slag is further worked up with coke in a small blast furnace. Some more tin can be recovered by this technique. The fused mass of tin and the impurities is allowed to flow along an inclined floor. The tin flows into a container while the impurities remain on the floor.

Uses : Tin has a great demand in packaging food materials. Lead-tin alloy is used in the construction of cheap roof and sheds. It is also used in the construction of gasoline tanks. Tin also is a constituent of solder, brass, bronze etc. alloys.

18.9. LEAD

18.9.1. Some Compounds of Lead : Lead has a variety of interesting compounds. Fig. 18.5 depicts an outline of the syntheses of several bivalent lead compounds. Below we describe a few chosen lead (II) and lead (IV) compounds.

Lead Monoxide : This also goes by the name *litharge*. This is usually prepared by blowing air over molten lead. It is also obtained by thermal decomposition of lead carbonate. It is a light yellow substance which is insoluble in water but soluble in both acids and alkalies :

$$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O$$
$$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O$$

Red Lead : This red coloured oxide is obtained by heating lead monoxide to around 300°C in a current of air :

$$6PbO + O_2 \rightleftharpoons 2Pb_3O_4$$

On heating to still higher temperature there is a tendency of Pb_3O_4 reverting back to PbO. It is an oxidant :

$$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + 4H_2O + Cl_2$$

The compound finds use in glass industry and as a red pigment.

Lead Dioxide : This black coloured oxide of lead may be obtained by sodium hypochlorite oxidation of a lead (II) salt in alkaline medium :

$$PbCl_2 + NaOCl + 2NaOH \rightarrow PbO_2 + 3NaCl + H_2O$$

Red lead may also be oxidised by concentrated nitric acid :

$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

The following reactions show that PbO_2 is a strong oxidant :

$$2MnSO_4 + 5PbO_2 + 6HNO_3 \rightarrow 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O$$

$$2Cr(OH)_3 + 10KOH + 3PbO_2 \rightarrow 2K_2CrO_4 + 3K_2PbO_2 + 8H_2O$$

$$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$$

On heating PbO_2 decomposes to Pb_3O_4 and oxygen :

$$3PbO_2 \xrightarrow{\sim 400^\circ C} Pb_3O_4 + O_2$$

It is used in match industry and as an oxidant in the laboratory.

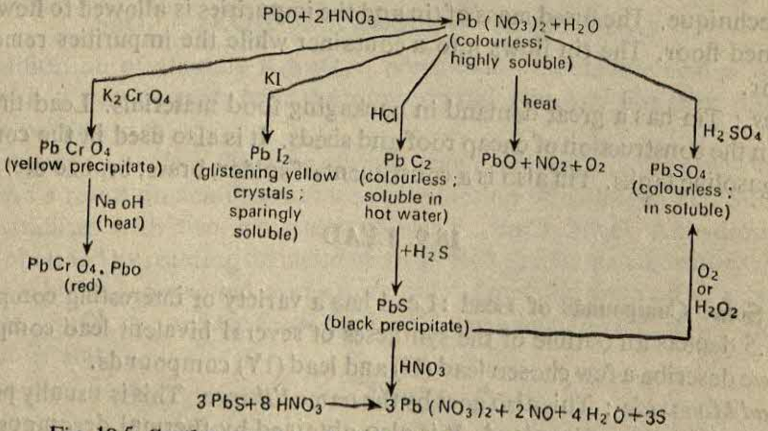


Fig. 18.5. Syntheses and reactions of lead (II) compounds

Lead Acetate and Basic Lead Acetate : PbO reacts with acetic acid to give a solution of lead acetate. On concentration crystals of $Pb(CH_3COO)_2$ are obtained. Aqueous solution of $Pb(CH_3COO)_2$ reacts with PbO under boiling to give basic lead acetate $Pb(CH_3COO)_2.2Pb(OH)_2$. Lead acetate is used in the laboratory as a reagent to detect sulphide ion and to precipitate chromate as lead chromate.

White Lead : White lead is a basic lead carbonate $2PbCO_3.Pb(OH)_2$. This is precipitated on the addition of alkali metal carbonate to an aqueous solution of lead salt. This precipitate has poor covering power. But white lead of commerce has a very satisfactory covering power and is in demand as a white pigment. Its commercial synthesis involves reaction of metallic lead with carbon dioxide and air in the presence of acetic acid.

For commercial manufacture the above reactions are allowed to proceed slowly over a period of about 100 days. The process is popularly known as *stack* *process*. The reaction chambers are made of brick and are usually 15 feet by 15 feet and another 20–25 feet in height. A layer of moist oak barks about 3 feet in depth is first laid out. On this oak bark bed are placed several earthenware pots containing acetic acid. Over these pots are placed perforated lead sheets one over another to a thickness of about 5–6 inches. In the brickwork chambers there are arrangements for having several such layers of oak bark, earthen pots with acetic acid and perforated lead sheets. The oak barks undergo fermentation, thereby raising the temperature and evolving carbon dioxide and moisture. It is believed that heat, moisture and oxygen first produce lead hydroxide which then reacts with acetic acid to form the basic lead acetate. The reactions may be represented in the following simplified form :

$$2Pb + 2CH_3COOH + O_2 \rightarrow 2Pb(OH)(CH_3COO)$$

$$3Pb(OH)(CH_3COO) + 2CO_2 + H_2O \rightarrow Pb(OH)_2.2PbCO_3 + 3CH_3COOH$$

The basic lead acetate alongwith the unconverted lead sheets are removed washed with water and the white lead collected. It forms a fine white paint when used with linseed oil. However it gets blackened in an atmosphere of H_2S. This is due to the formation of PbS.

Lead Tetraacetate : Red lead, Pb_3O_4, reacts with acetic acid at 60°C to form lead (II) acetate and lead (IV) acetate. Acetic anhydride is used during the synthesis to remove the liberated water and thereby to suppress any hydrolysis of lead tetraacetate :

$$Pb_3O_4 + 8CH_3COOH \rightarrow Pb(CH_3COO)_4 + 2Pb(CH_3COO)_2 + 4H_2O$$

$$Pb(CH_3COO)_4 + 2H_2O \rightarrow PbO_2 + 4CH_3COOH$$

On cooling the solution lead tetraacetate crystallises out. This is a very effective oxidant. It oxidises chloride, bromide and iodide to the respective halogens. Alcohol is oxidised to aldehyde.

Anodic oxidation of lead (II) acetate in anhydrous acetic acid medium also gives crystals of lead tetraacetate at the anode.

Tetraalkyl Lead : It is prepared by the reaction of sodium (1 %)—lead alloy and ethyl chloride (C_2H_5Cl). Pyridine is used as a catalyst in this reaction. This can also be obtained by electrolysis of alkyl (ethyl) magnesium chloride using lead anode. The major use of tetraalkyl lead is as an antiknock compound added to the gasolene in automobile engines. This raises the efficiency of the engines by reducing the mild explosions or knocks inside the engine.

18.9.2. Industrial Preparation of Lead : The important ores of lead are galena (PbS), cerussite ($PbCO_3$) and anglesite ($PbSO_4$). The amount of lead present in these ores is rather small because of large quantities of impurities. The very first step is therefore concentration of the ore. The concentration of galena is done by the froth floatation process (Chapter 13). Finely powdered galena is thoroughly mixed with water and turpentine oil or similar such oil and the mixture is agitated by blowing air through. Enough froth is thereby generated and most of the galena floats up with the froth. Silica and other undesirable impurities settle down and can be removed easily.

Enriched galena is mixed with coke and limestone and heated in the presence of air. Gaseous products escape through an opening at the top of the roasting furnace. Galena is thereby converted to lead monoxide :

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

$$C + O_2 \rightarrow CO_2$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$PbO + SO_3 \rightarrow PbSO_4$$

The above reactions are exothermic and hence help in maintaining the desired temperature inside the roasting furnace. As a result of the roasting PbS, $PbSO_4$, PbO are converted into small particles.

The roasted material is mixed with further amounts of limestone, coke and small amount of iron ore and then the mixture is heated in a small blast furnace. The following reactions take place:

$$PbO + CO \rightarrow Pb + CO_2$$

$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2$$

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$

$$FeO + PbS + C \rightarrow Pb + FeS + CO$$

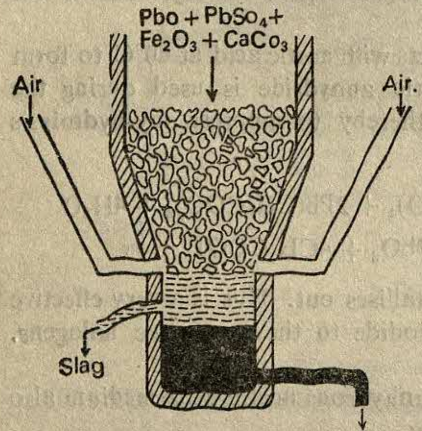


Fig. 18.6. Recovery of lead in blast furnace

The fused lead collects below the fused slag. The lead and the slag are drawn out of the blast furnace through two tap holes. The slag consists of mainly calcium silicate and iron sulphide.

The lead obtained by the above procedure is not quite pure. It is further purified by electrolytic procedure. Impure lead plates serve as anodes while plates of pure lead are made the cathodes of the electrolytic cell. A solution of $PbSiF_6$ and H_2SiF_6 is used as the electrolyte. On electrolysis lead dissolves at the anode to give lead (II) ions while impurities like copper, antimony etc. deposit below the anode as anode sludge. The lead (II) ions are reduced at the cathode and are deposited as pure lead metal.

at the anode : $Pb \rightarrow Pb^{2+} + 2e$

at the cathode : $Pb^{2+} + 2e \rightarrow Pb$

Properties and Uses : Lead (II) sulphate, carbonate are insoluble in water. Soluble lead (II) salts are very harmful to human being. The drinking water supplied by the municipalities is usually hard water. During transport through lead pipes there develops a coating of the insoluble lead (II) carbonate and sulphate on the inside surface of the pipes. Thus the drinking water does not come much in contact with the lead metal of the pipes. In the case of soft water it will be medically unwise to use lead pipes for transportation of drinking water.

Lead Alloys : These have already been mentioned under tin.

Lead Storage Battery or Lead Accumulator : These batteries serve as a ready source of current in our laboratories, in automobiles and a variety of other cases. These batteries are made of a series of alternate cathode and anode plates. Cathodes are lead plates over which there is a coating of PbO_2 while the anodes are lead plates alone. These plates are immersed in $9-10N$ H_2SO_4 solution. We recollect that anodes are the plates where oxidation i.e. release of electrons occurs. On the contrary reduction occurs at the cathodes. The anodes are connected to form a terminal and this is marked black. The cathodes are again connected to form another terminal and this is marked red. When such a cell is required to supply current the negative terminal i.e. the black one is connected to the cathode of an electrolytic cell while the positive terminal i.e. the red one is connected to the anode of the electrolytic cell. When the lead storage battery supplies current it functions as an electrochemical cell. During supply of current the following reactions occur within the battery :

$$\begin{array}{rr} \textit{at the anode (black terminal)}: & Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e \\ \textit{at the cathode (red terminal)}: & PbO_2 + 4H^+ + SO_4^{2-} + 2e \rightarrow PbSO_4 + 2H_2O \\ \hline \text{Over-all reaction}: & Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O \end{array}$$

As we continue to draw current from the battery there develop layers of $PbSO_4$ on both the electrode plates. This results in reduction of the concentration of H_2SO_4 in the cell i.e. in the electrolyte. The consequent result is a fall in the potential of the cell from its original value (usually 2 volts). The cell can be brought back to its original activity by making it now an electrolytic cell and by passing current through it from an external source of higher voltage. The anode of the battery (i.e. the black terminal) is now connected to an external terminal supplying electrons (i.e. a negative terminal) and the cathode of the battery (i.e. the red terminal) is connected to an external terminal taking off electrons (i.e. a positive terminal). Under these conditions reverse reactions will take place at the cathode and the anode of the battery :

$$\begin{array}{lr} \textit{at the anode}: & PbSO_4 + 2e \rightarrow Pb + SO_4^{2-} \\ \textit{at the cathode}: & PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e \\ \hline & 2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \end{array}$$

An interesting point that should be noted is that the lead accumulators act as electrochemical cells while serving current but as electrolytic cells while being regenerated. During supply of current these are slowly *discharged* but while being regenerated these are said to be *charged*. Thus these batteries may be used over and over again. From time to time some water is added in order to stop drying up of the battery.

EXERCISES

1. Present a comparative study of the group IVB elements of the periodic table.

2. What is inert pair effect? Discuss this effect as you have found it to influence the chemistry of the elements belonging to group IVB.

3. Write an essay on the allotropic modifications of carbon.

4. Give an account of the diagonal relationship of boron and silicon.

5. Starting from carbon how would you prepare the following compounds :
(*a*) water gas (*b*) producer gas (*c*) silicon carbide (*d*) carbon disulphide (*e*) $Ni(CO)_4$

6. Explain the nature of bonding in (*a*) diamond (*b*) carbon monoxide (*c*) carbon dioxide (*d*) silica (*e*) silicon carbide

7. Bring out the similarities in the nature of bonding in binary carbides and binary hydrides. Describe the properties of the different forms of binary carbides.

8. Give in outline the syntheses of the following beginning with silica :
(*a*) silicon (*b*) water glass (*c*) silicochloroform (*d*) silane (*e*) carborundum (*f*) hydrofluosilicic acid

9. Beginning with PbO how would you prepare the followng?
(*a*) lead nitrate (*b*) lead iodide (*c*) lead chromate (*d*) lead chloride

10. Give a comparative assessment of the chemistry of tin and lead.

11. Write short notes on :
(*a*) white lead (*b*) lead tetraacetate (*c*) lead dioxide (*d*) stannous chloride (*e*) stannic chloride (*f*) mosaic gold (*g*) glass

12. Complete the following reactions :

(*a*) $SiO_2 + C \rightarrow$

(*b*) $CaF_2 + H_2SO_4 + SiO_2 \rightarrow$

(*c*) $SiO_2 + HF \rightarrow$

(*d*) $SiF_4 + H_2O \rightarrow$

(*e*) $Sn + HNO_3 \rightarrow$

(*f*) $MnSO_4 + PbO_2 + HNO_3 \rightarrow$

CHAPTER 19

GROUP VB. NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY AND BISMUTH

19.1. INTRODUCTION

This group consists of the elements nitrogen, phosphorus, arsenic, antimony and bismuth. We observe that the general group trends are found to be valid here too. Since this group is closer to the halogen family we find a general increase in their electronegativities. This results in an increase in nonmetallic character. Again in keeping with the increase in metallic character with increasing atomic number we find that while nitrogen and phosphorus are entirely nonmetallic, arsenic and antimony are metalloids and bismuth is entirely metallic.

19.2. A COMPARATIVE STUDY OF THE GROUP VB ELEMENTS

Physical Properties : 1. All the five elements of this group have similar electron distributions in their outermost shells namely s^2p^3. All these elements are representative elements and have been included in group VB by virtue of their having five electrons in their outer levels.

2. It is a common experience that as we go down a group of elements there is a decrease in the ionisation potentials. In keeping with this trend there is a fall in the I.P. values as we move from nitrogen to bismuth (Table 19.1).

3. In keeping with expected variation we find that electronegativity also falls from nitrogen to bismuth.

4. With increasing atomic number the size of the atoms in a particular group increases. This is reflected in an increase in the covalent/atomic radii of the elements.

5. Although the elements have a total of five electrons in the two subshells those in the *s* subshell may remain inert in some chemical reactions. For this reason we find that the elements exhibit two valences : 3 and 5. In their trivalent state the two *s* electrons remain inert and are said to form an *inert pair*.

Table 19.1. A Comparison of Group VB Elements

Element	Atomic Number	Electron Distribution	Ionisation Potential (*ev*)	Atomic Radius(A)	Electro-negativity	Melting Point (°C)
N	7	[He]$2s^22p^3$	14.53 29.59 47.42 77.45 97.86	0.70	3.0	−210

Table 19.1. (*Continued*)

P	15	$[Ne]3s^2 3p^3$	10.48 19.72 30.15 51.35 65.00	1.06	2.1	44
As	33	$[Ar]3d^{10} 4s^2 4p^3$	9.81 18.63 28.34 50.10 62.60	1.19	2.0	817 (36 atm)
Sb	51	$[Kr]4d^{10} 5s^2 5p^3$	8.64 16.50 25.30 44.10 56.00	1.38	1.9	630
Bi	83	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$	7.29 16.68 25.56 45.30 56.00	1.46	1.9	271

6. As expected the densities of the elements increase with increasing atomic number :

	nitrogen	phosphorus	arsenic	antimony	bismuth
density(gm/ml)	1.03	1.83	5.7	6.6	9.8

Chemical Properties : 1. The hydrides of these elements belong to the category of covalent hydrides. All the hydrides are gaseous in nature : NH_3, N_2H_4, PH_3, AsH_3 etc. As we move from nitrogen to bismuth down the series the thermal stability, hydrogen bonding ability and basic properties fall off but reducing ability increases.

2. Of these elements nitrogen alone gives a trihalide while the others can give both trihalides and pentahalides. It should be appreciated that nitrogen being a member of the second period of the table its valence shell is restricted to only eight. As a result it is not possible for the element to give a pentahalide which would require expansion of its valence shell to ten electrons. Compared to nitrogen trihalide the halides of the other elements are readily hydrolysed because of availability of *d* orbitals. H_2O molecules can easily make nucleophilic attack on the vacant *d* orbitals thus bringing about hydrolysis.

3. These elements give a variety of oxides. As the oxidation number increases the acid character increases. Thus N_2O_5 is a stronger acidic oxide than N_2O_3. Again having the same oxidation number acid character decreases with increasing atomic number : $N_2O_3 > P_4O_6 > As_4O_6 > Sb_4O_6 > Bi_2O_3$, In the oxidation number 3 nitrogen oxide is wholly acidic, oxides of arsenic and antimony are amphoteric and bismuth oxide is basic.

19.3. THE MOLECULAR STATES

Nitrogen forms a diatomic molecule. In order to attain the stability of a noble gas there should be multiple bonds between the two atoms. In fact there is a triple bond between the two atoms. Of these one is a sigma type bond and the other two are of the pi type. Assuming a simplified version of the bonding we take the overlap of the two p_x orbitals (with one electron on each) to generate the sigma bond. Overlap of the p_y of one with the p_y orbital of the other forms the first pi bond. The second pi bond is formed by the overlap of the remaining p_z orbitals. That in the N_2 molecule there is a triple bond is revealed by an inspection of the bond lengths. N–N single bond length is known to be 1.5A. N = N double bond length is 1.2A but that in the N_2 molecule is around 1.1A.

The allotropic modifications of phosphorus have already been discussed in Chapter 10. In the other three elements the atoms are sp^2 hybridised and each atom is linked to three others. Thus a planar hexagonal polymeric structure results. Each of the atoms is left with a lone pair of electrons on the third *p* orbital. The structure is somewhat comparable to that of graphite. Like graphite here too there exists a weak van der Waals force in between the layers. Tetrahedral monomeric structure like P_4(Chapter 10) are obtained in arsenic and antimony when their vapours are rapidly cooled. The tetrameric forms As_4 and Sb_4 are highly reactive.

19.4. ACTIVE NITROGEN

When molecular nitrogen is subjected to electric discharge under low pressure there appears a yellow glow which persists for some time even after the discharge is stopped. It is now known that the yellow glow is due to break down of molecular nitrogen to atomic nitrogen. However atomic or so called active nitrogen is quite short lived and recombines to form stable, inert molecular nitrogen.

Active nitrogen can bring about some reactions which are not possible by molecular nitrogen. At ordinary temperature it reacts with mercury to form mercury nitride. Similar nitrides are also formed with phosphorus, sulphur and iodine. The formulas of many of these reaction products are not known with certainty. The product with sulphur is believed to be $(NS)_x$. Reaction with hydrocarbon produces HCN. It converts NO to NO_2 and N_2 :

$$2CH_4 + 2N \rightarrow 2HCN + 3H_2$$
$$2NO + N \rightarrow NO_2 + N_2$$

19.5. HYDRIDES OF NITROGEN

The three important hydrides are : (a) ammonia (b) hydrazine and (c) hydrazoic acid.

19.5.1. Ammonia : A variety of methods are available for its preparation in laboratory and on industrial scale. Fig. 19.1 gives a flowsheet diagram of the various preparative methods.

Laboratory Method : It is obtained by the reaction of ammonium salts with NaOH or by dropping liquor ammonia on solid NaOH :

$$NH_4Cl + NaOH \rightarrow NH_3 + H_2O + NaCl$$
$$NH_4OH + (NaOH) \rightarrow NH_3 + H_2O + (NaOH)$$

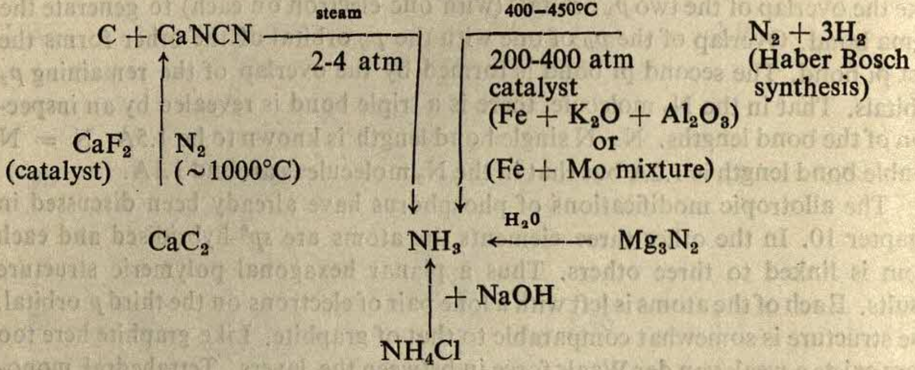


Fig. 19.1. Flow sheet diagram for the various methods of syntheses of ammonia

Cyanamide Method : Nitrogen of air can be converted to cyanamide of calcium from which we can obtain ammonia. Conversion of aerial nitrogen to useful products of commerce is known as fixation of atmospheric nitrogen.

Nitrogen of air is made to react with calcium carbide in an electric furnace at a temperature of about 1000°C. Calcium fluoride is used in this reaction as a catalyst. The calcium cyanamide so produced is forced to react with steam under 2-4 atmosphere pressure. Ammonia is formed alongwith insoluble $CaCO_3$. The $CaCO_3$ is decomposed at 1000°C to CO_2 and CaO. The quicklime is then reacted with coke at ~ 3000°C to get CaC_2. Thus the same $CaCO_3$ can be used over and over again.

$CaC_2 + N_2 \rightarrow CaNCN + C$ (the mixture of CaNCN and C is known as nitrolim)

$$CaNCN + 3H_2O \xrightarrow[\text{pressure}]{\text{steam}} 2NH_3 + CaCO_3$$

Nitrolim (CaNCN + C) is used as a fertiliser. The calcium cyanamide reacts with CO_2 and moisture of the atmosphere to form urea ($NH_2{-}CO{-}NH_2$) which is then hydrolysed to ammonia and carbonic acid.

$$\begin{tikzcd} & CaNCN + H_2O + CO_2 \arrow[r] & CaCO_3 + H_2N.CN \arrow[d, "H_2O"] \\ & 2NH_3 + H_2CO_3 & NH_2{-}CO{-}NH_2 \arrow[l, "2H_2O"'] \end{tikzcd}$$

Haber — Bosch Synthesis : Prior to the first world war the demand for nitrates and other nitrogenous compounds in Germany used to be met from imports from abroad. Due to the war this supply was totally suspended. But the demand for nitrogenous materials particularly for making explosives, bombs etc. during war time was too high. Germany needed enough of ammonia, nitric acid etc. Haber and Bosch solved the problem by fixing atmospheric nitrogen as ammonia. The following synthetic reaction is exothermic :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 22.0\ \text{KCal}$$

The reaction besides being exothermic leads to a reduction in volume. The reaction attains equilibrium and optimum conditions have to be properly set in order to get the best yield of ammonia. Le Chatelier principle helps us to draw some conclusions about how to get the best yield. This principle states : *When a system attains equilibrium any constraint imposed from outside is resisted so as to minimise the effect of the imposed constraints.* The reaction is exothermic. If we apply heat to the system at equilibrium the system will tend to minimise the effect of imposed heat. This the system can best do by absorbing some of the applied heat i.e. by taking the reaction from right to left because the heat content of the mixture (N_2+3H_2) is more than that of NH_3. So increasing temperature will decrease the yield of NH_3. The reaction indicates a decrease in volume from left to right. If we increase pressure when the system is at equilibrium the system will again tend to minimise the effect of imposed pressure. This can be done by reducing the volume i.e. by converting more of the mixture to ammonia of smaller volume. Thus the effect of applied pressure will be somewhat neutralised. Thus increasing temperature and pressure have opposing effect on the equilibrium. A compromise has been found by operating at 400-450°C and at 200-400 atm. pressure. Over and above a catalyst, usually a mixture of powdered iron, potassium oxide and aluminium oxide or a mixture of finely divided iron and molybdenum is used to optimise formation of NH_3.

The two ingredients, namely nitrogen and hydrogen, must be quite pure. Hydrogen is usually obtained from electrolysis of water while nitrogen is collected out of fractional distillation of liquid air. An alternative source is producer gas ($CO + N_2$), water gas and steam in right proportion. This mixture is passed over a heated catalyst ($Fe_2O_3 + Cr_2O_3$) :

$$(CO + N_2) + (H_2 + CO) + 2H_2O \xrightarrow[\text{heat}]{Fe_2O_3+Cr_2O_3} 2CO_2 + 3H_2 + N_2$$

The issuing gas mixture is led through water under pressure when CO_2 dissolves out. Any unconverted CO is absorbed in ammoniacal cuprous chloride.

The catalyst chambers are usually made of chrome steel and have several racks. Small pieces of the catalyst are spread out on these racks and temperature is controlled electrically. The mixture of the pure gases in the ratio $1N_2 : 3H_2$ is led under pressure through the catalyst bed and the gas coming out is cooled sufficiently to liquefy ammonia (B.P. −33°C). The unconverted mixture of nitrogen and hydrogen is further treated with fresh nitrogen and hydrogen and the reaction continued.

Structure of Ammonia : The bond angles $<H-N-H$ in ammonia are all around 107°C. This means that the compound has a tetrahedral stereochemistry. Nitrogen has thus sp^3 hybrid orbitals. One of these four hybrid orbitals has the

lone pair while the other three have an unpaired electron on each. These three hybrid orbitals overlap with the 1*s* electrons of the three hydrogen atoms to form the NH_3 molecule. (Chapter 5).

Properties and Uses : Ammonia is a weak base. It forms NH_4OH in water. The gas reacts with acids to form salts like NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3 etc. It can be oxidised in the presence of hot platinum gauze to NO which may be converted further in presence of oxygen to NO_2. From this NO_2 we can have HNO_3 by further oxidation followed by reaction with water :

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$

The dry gas reacts with sodium metal to give sodamide :

$$2NH_3 + 2Na \rightarrow 2NaNH_2 + H_2$$

It is oxidised by chlorine gas to nitrogen :

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

The most important use of ammonia is as a fertiliser actually used in the form of salts like ammonium sulphate, ammonium phosphate etc. It is also used in the manufacture of sodium carbonate by Solvay process. It is also used in the manufacture of nitric acid. Liquid ammonia finds use in the manufacture of ice.

Some Ammonium Salts : Some important ammonium salts of commerce are described below:

Ammonium Sulphate : It is now in great demand as a fertiliser. In our country there is not enough deposit of sulphur for production of H_2SO_4. Because of this the simple reaction of neutralisation of ammonia by H_2SO_4 is not made use of commercially for the preparation of this fertiliser. We have good deposit of gypsum, $CaSO_4.2H_2O$. A slurry of gypsum is made with water and through this slurry a stream of CO_2 and NH_3 is passed. Ammonium sulphate is produced in solution while $CaCO_3$ appears as the insoluble material.

$$CaSO_4(2H_2O) + 2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2SO_4 + CaCO_3 \downarrow + (2H_2O)$$

The insoluble $CaCO_3$ is removed and the solution is concentrated to obtain crystals of ammonium sulphate. Calcium carbonate is either sent to cement factory or sometimes used as a fertiliser.

Ammonium Carbonate and Bicarbonate : We have already noted in Chapter 15 that according to the Solvay process ammonia and carbon dioxide react to form the bicarbonate :

$$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$$

This ammonium bicarbonate is converted to ammonium carbonate on treatment with more ammonia :

$$NH_4HCO_3 + NH_4OH \rightarrow (NH_4)_2CO_3 + H_2O$$

Ammonium carbonate finds use as a smelling salt. In air it decomposes :

$$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O$$

Sodium Ammonium Hydrogen Phosphate : Another name of this compound is microcosmic salt. A 1 : 1 mixture of NH_4Cl and Na_2HPO_4 is dissolved in water and the solution concentrated. NaCl crystallises out first and filtered off. The filtered solution is concentrated to get crystals of microcosmic salt. On heating the compound loses water and ammonia and gives sodium hexametaphosphate :

$$\begin{tikzcd} NH_4Cl + Na_2HPO_4 \arrow[r] & NaCl + Na(NH_4)HPO_4 \arrow[d] \\ {[NaPO_3]_6} & Na(NH_4)HPO_4.4H_2O \text{ (hydrated crystals)} \arrow[l, "\text{heat}"'] \end{tikzcd}$$

Sodium hexametaphosphate is sometimes used in softening of hard water :

$$Na_2[Na_4(PO_3)_6] + CaSO_4 \rightarrow Na_2[Na_2Ca(PO_3)_6] + Na_2SO_4$$

Many metal oxides give characteristically coloured phosphate beads :

$$NaPO_3 + CuO \rightarrow CuNaPO_4 \text{ (blue-green)}$$

These phosphate beads are of help in the qualitative detection of metal ions.

Ammonium Polysulphide : When H_2S is passed through a solution of ammonia we get$(NH_4)_2S$. When this solution is treated with powdered sulphur and more H_2S the colour turns yellow-red due to the formation of polysulphide :

$$(NH_4)_2S + 2S \rightarrow (NH_4)_2S_3 \ ; \ (NH_4)_2S + (n-1)S \rightarrow (NH_4)_2S_n$$

This polysulphide dissolves the precipitates of As_2S_3, Sb_2S_3 to give soluble thioarsenate and thioantimonate :

$$3(NH_4)_2S + As_2S_3 + 2S \rightarrow 2(NH_4)_3AsS_4$$

On acidification of such solutions antimony/arsenic pentasulphides (As_2S_5/Sb_2S_5) are precpitated.

19.5.2. Hydrazine : It is an oxidised product of ammonia. Oxidation of ammonia is carried out by sodium hypochlorite in the presence of gelatin :

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH \ ; \ NH_2Cl + 2NH_3 \rightarrow N_2H_4 + NH_4Cl$$

The purpose of gelatin is to stop the oxidation of ammonia beyond N_2H_4 i.e. not to allow the reaction to go upto N_2 :

$$N_2H_4 + 2NH_2Cl \rightarrow N_2 + 2NH_4Cl$$

At the end of the reaction with hypochlorite the reaction product is cooled in ice, treated with dilute H_2SO_4 and crystals of hydrazine sulphate, $N_2H_4.H_2SO_4$, are collected. On basification by NaOH hydrazine hydrate, $N_2H_4.H_2O$, is formed. On careful distillation under reduced pressure pure hydrazine, N_2H_4, is obtained. Melting point and boiling points of hydrazine are 2°C and 114°C respectively.

Hydrazine is a good reducing agent. It reduces ferric to ferrous, halogens to respective halides and iodate to iodide :

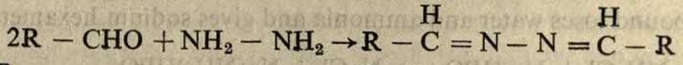
$$N_2H_4 + 4FeCl_3 \rightarrow N_2 + 4FeCl_2 + 4HCl$$

$$N_2H_4 + 2Cl_2 \rightarrow N_2 + 4HCl$$

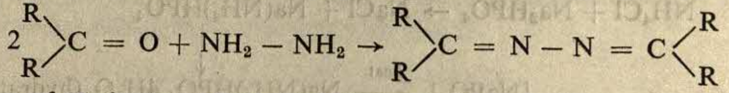
Hydrazine can be reduced to NH_3 by the action of zinc and hydrochloric acid.

$$N_2H_4 + Zn + 2HCl \rightarrow 2NH_3 + ZnCl_2$$

Hydrazine reacts with organic aldehyde and ketones to give aldazine and ketazine respectively :



$$2R - CHO + NH_2 - NH_2 \rightarrow R - \overset{H}{C} = N - N = \overset{H}{C} - R$$



Structure of Hydrazine : Both the nitrogens in hydrazine are tetrahedral. Each nitrogen is linked to two hydrogens and the other nitrogen by single bonds. Besides, on each nitrogen there remains a lone pair of electrons. But the stereo-chemical directions of the lone pairs are such that they cannot occupy *cis* positions about a central metal atom. Hence the compound cannot function as a bidentate ligand. But the lone pairs can bind two metal ions, thus functioning as a bridging ligand. Hydrazine thus can behave as either (a) a monodentate donor or (b) as a bridging ligand between two metal ions. (Fig. 19.2)

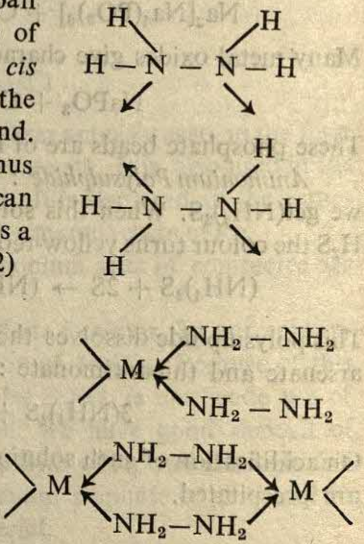


Fig. 19·2, Structure and bonding character of N_2H_4

19.5.3. Hydrazoic Acid (Hydrogen Azide) : Around 200°C sodium and ammonia react to give sodamide $NaNH_2$. Then at about the same temperature a reaction is carried out between sodamide and N_2O. Dry N_2O is used to chase the gases H_2 and NH_3:

$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$$
$$NaNH_2 + N_2O \rightarrow NaN_3 + H_2O$$
$$NaNH_2 + H_2O \rightarrow NaOH + NH_3$$

After the evolution of ammonia ceases the mixture is cooled and acidified with dilute H_2SO_4 and then distilled under reduced pressure. An aqueous solution of HN_3 is produced. If this solution is treated with anhydrous $CaCl_2$ and again distilled we get anhydrous HN_3 which is quite an explosive. Its boiling point is 37°C and is a very weak acid ($K_A \sim 10^{-5}$). Its many properties resemble those of the halogens and hence it is often termed as a pseudohalogen. It shows properties characteristic both of an oxidant and a reductant :

as an oxidant : $HN_3 + 4H_2 \rightarrow 3NH_3$

as a reductant : $2HN_3 + \frac{1}{2}O_2 \rightarrow 3N_2 + H_2O$

Structure of Hydrazoic Acid : Both the acid and the anion can have several resonating structures :

$$H-N = \overset{+}{N} = \overset{-}{N} \longleftrightarrow H-\overset{-}{N}-\overset{+}{N} \equiv N$$

$$\overset{-}{N} = \overset{+}{N} = \overset{-}{N} \longleftrightarrow N \equiv \overset{+}{N}-\overset{--}{N} \longleftrightarrow \overset{--}{N}-\overset{+}{N} \equiv N$$

As we have observed in Chapter 5 the real structure will be a resonance hybrid of the above forms.

19.6. HYDROXYLAMINE

The formula of the compound is NH_2OH. This shows that one of the hydrogen atoms of NH_3 has been replaced by a hydroxyl group. The compound can be obtained by two methods :

1. *Reduction of Nitrite by Sulphite* :

$$HO.NO(\sim HNO_2) + 2Na_2SO_3 \longrightarrow HO.N(SO_3Na)_2 + Na_2O$$

$$HO.N(SO_3Na)_2 + 2H_2O \xrightarrow[90^{\circ}C]{H_2SO_4} HO.NH_2.H_2SO_4 + Na_2SO_4$$

2. *Electrolysis of HNO_3 using lead cathode* : A diaphragmed cell is used. A mixture of 50 % HNO_3 and 50 % H_2SO_4 is used as the electrolyte. Cathode material is lead where hydrogen has a high overvoltage i.e. hydrogen atoms exist for quite sometime to effect the reduction. The electron on the cathode surface attaches to hydrogen ion to form hydrogen atom which then brings about the reduction of HNO_3 to hydroxylamine. The reaction is usually expressed in the following form:

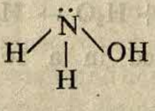
$$HONO_2 + 6H^+ + 6e \rightarrow HO.NH_2 + 2H_2O$$

Hydroxylamine is less basic than ammonia. On replacing one of the hydrogen atoms of NH_3 by an $-OH$ group nitrogen gets attached to a more electronegative oxygen. This results in a lowering of overall electron density on nitrogen, thereby making hydroxylamine a weaker base. Hydroxylamine also exhibits both oxidising and reducing properties :

as an oxidant : $2Fe(OH)_2 + NH_2OH + H_2O \rightarrow 2Fe(OH)_3 + NH_3$

as a reductant : $2NH_2OH + 4CuO \rightarrow N_2O + 2Cu_2O + 3H_2O$

Structure of Hydroxylamine : Its may be represented by the following structure :



19.7. OXIDES OF NITROGEN :

Oxidation number, formula, boiling point, decomposition and acid properties of the different oxides of nitrogen are shown below :

oxidation number :	+1	+2	+3	+4	+5
formula :	N_2O	NO	N_2O_3	$NO_2(N_2O_4)$	N_2O_5
boiling point (°C) :	−88	−152	3.5 (decomp.)	2.1 (decomp.)	47 (decomp.)

acidic properties increase in this direction

19.7.1. Nitrous Oxide : This oxide of nitrogen is obtained by heating ammonium nitrate to about 200°C :

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

Nitric oxide, NO, is also evolved as an impurity. This is removed by absorbing in a solution of ferrous sulphate as $FeSO_4.NO(5H_2O)$. Nitrous oxide is rather inert. It does not undergo any reaction with halogens, alkali metals or ozone. This is a neutral oxide. No $H_2N_2O_2$ is produced in water indicating that it is really a neutral oxide. It suffers thermal decomposition at about 600°C to furnish nitrogen and oxygen:

$$2N_2O \rightarrow 2N_2 + O_2$$

In the olden days this oxide was known as laughing gas as it produced laughing on inhaling.

Structure of N_2O : It is a linear compound. It is a resonance hybrid of the following forms :

$$:\overset{-}{\ddot{N}} = \overset{+}{N} = \ddot{O}: \longleftrightarrow :N \equiv \overset{+}{N} - \underset{..}{\overset{-}{\ddot{O}}}:$$

19.7.2. Nitric Oxide : Its industrial preparation involves oxidation of ammonia by oxygen at about 500°C over a platinum catalyst:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

NO can also be obtained by the reduction of nitrite or nitrate:

$$2NaNO_3 + FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$$

$$8HNO_3 + 3Cu \rightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$$

NO is a neutral oxide. The oxidation number of nitrogen in this oxide is + 2 and hence it can be oxidised further. In air it is oxidised to brown NO_2. It reacts with halogens to produce NOF, NOCl etc :

$$2NO + Cl_2 \rightarrow 2NOCl$$

In the presence of strong oxidants it is oxidised to N_2O_5, which gives with water HNO_3. It is reduced by SO_2 to N_2O :

$$2NO + SO_2 + H_2O \rightarrow H_2SO_4 + N_2O$$

Nitric oxide is readily absorbed in a solution of $FeSO_4$ giving brown $FeSO_4NO.\ 5H_2O$:

$$FeSO_4 + NO + 5H_2O \rightarrow FeSO_4.NO.5H_2O$$

It is one of the few odd electron compounds known. Its structure may be represented as a resonance hybrid of the following:

$$:\dot{N}=\ddot{O}: \longleftrightarrow :\overset{-}{\ddot{N}}=\overset{\cdot +}{O}:$$

The odd, unpaired electron can be easily removed from the compound. The resulting nitosyl cation is known to exist in several compounds :

$$N_2O_3 + 2H_2SO_4 \rightarrow 2NOHSO_4 + H_2O$$

$$N_2O_3 + 2HClO_4 \rightarrow 2NOClO_4 + H_2O$$

In nitrosyl bisulphate or nitrosyl perchlorate NO^+ cation is present. Because of the presence of the odd, unpaired electron the compound NO is paramagnetic.

19.7.3. Nitrogen Sesquioxide/Dinitrogen Trioxide : Mixing of NO and NO_2 in 1 : 1 ratio gives this oxide. On mixing dilute HNO_3 with As_2O_3 followed by distillation N_2O_3 is obtained in the form of a gas. This can be cooled to a blue liquid :

$$As_2O_3 + 2HNO_3 + 2H_2O \rightarrow N_2O_3 + 2H_3AsO_4$$

The oxide may be viewed as the anhydride of nitrous acid (HNO_2) :

$$N_2O_3 + H_2O \rightarrow 2HNO_2$$

In alkali solutions the oxide gives salts of alkali nitrites. HNO_2 and its salts function as reductants, reducing permanganate to manganese (II),

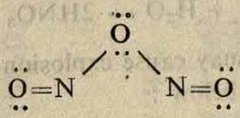
$$5NaNO_2 + 3H_2SO_4 + 2KMnO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5NaNO_3 + 3H_2O$$

On the other hand it can oxidise N_2O, NO, HI and ferrous ion :

$$2HI + 2HNO_2 \rightarrow 2H_2O + I_2 + 2NO$$

$$FeCl_2 + HNO_2 + HCl \rightarrow FeCl_3 + NO + H_2O$$

The following structure has been proposed for the compound :

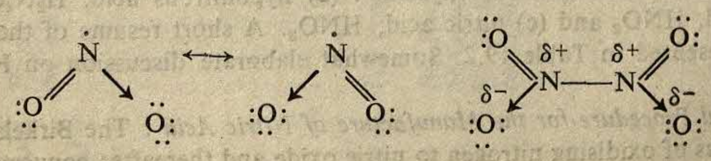


19.7.4. Nitrogen Dioxide/Dinitrogen Tetroxide : This oxide may occur either as monomer, NO_2, or a dimer N_2O_4. The red-brown gas that is evolved on heating heavy metal nitrates is the monomer NO_2 :

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

The gas can be cooled to give first the monomeric brown liquid NO_2. On cooling further a colourless liquid is obtained, which is the dimer N_2O_4.

NO_2 is an odd electron compound and hence is paramagnetic. But in the dimer the odd electrons pair up and hence it is diamagnetic. The structures are as shown below :



(actual N—O distance is 1.19A ;
calc. distance = sum of the two single bond
covalent radii = 0.70 + 0.66 = 1.36A;)

The actual and calculated bond distances in NO_2 tells us that the bonds have some double bond character justifying the proposed resonating structures shown above.

NO_2 dissolves in alkali solutions to give both nitrite and nitrate :

$$2KOH + 2NO_2 \rightarrow KNO_2 + KNO_3 + H_2O$$

Liquid N_2O_4 reacts with metals to give metal nitrate and gaseous NO :

$$K + N_2O_4 \rightarrow KNO_3 + NO$$

In solvents of high dielectric constants like $HClO_4$, H_2SO_4 the compound dissociates as follows :

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

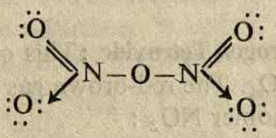
19.7.5. Dinitrogen Pentoxide : This can be obtained via dehydration of HNO_3 by P_4O_{10}.

$$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$$

The mixture of HNO_3 and P_4O_{10} is distilled in a stream of ozone. This may be viewed as the anhydride of HNO_3 :

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

The oxide is very unstable and may cause explosion. The structure of gaseous N_2O_5 is believed to be as shown below :



On sufficient cooling crystals of N_2O_5 may be obtained. In the crystalline state it is believed to be in the ionic form : $[NO_2]^+[NO_3]^-$

19.8. OXYACIDS OF NITROGEN

Nitrogen has three important oxyacids : (a) hyponitrous acid, $H_2N_2O_2$; (b) nitrous acid, HNO_2 and (c) nitric acid, HNO_3. A short resume of these three acids is presented in Table 19.2. Somewhat elaborate discussion on HNO_3 is made next.

Ostwald Procedure for the Manufacture of Nitric Acid : The Birkeland and Eyde process of oxidising nitrogen to nitric oxide and thereafter converting it to HNO_3 is very costly as it involves huge amount of electricity. On the contrary the Ostwald process of oxidising ammonia is cheaper and is the currently used method.

Table 19.2. A Comparative Study of the Oxyacids of Nitrogen

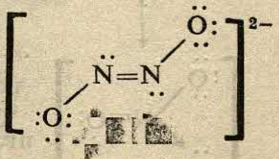
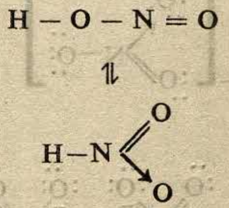
Acid and Formula	Preparative Procedure	Chemical Reactions during preparative procedure	Properties	Structure
Hyponitrous acid ($H_2N_2O_2$)	From $NaNO_2$	Formed by the reaction of $NaNO_2$ and sodium amalgam in water : $2NaNO_2 + 4H \rightarrow Na_2N_2O_2 + 2H_2O$ $\downarrow Ag^+$ $\downarrow AgCl + H_2N_2O_2 \xleftarrow{HCl} AgN_2O_2$ $\downarrow$ ether crystals of $H_2N_2O_2$	(a) weak acid ($K_A \sim 10^{-7}$ (b) reducing property $5H_2N_2O_2 + 8KMnO_4 + 12H_2SO_4 \rightarrow 10HNO_3 + 4K_2SO_4 + 8MnSO_4 + 12H_2O$ (c) unstable in solution $H_2N_2O_2 \rightarrow H_2O + N_2O$ (d) hyponitrite salts decompose on heating : $3Na_2N_2O_2 \rightarrow 2NaNO_2 + 2Na_2O + 2N_2$	$H_2N_2O_2$ has zero dipole moment. A *trans* configuration has been suggested : 
Nitrous acid (HNO_2)	(a) From N_2O_3 (b) Nitrites are formed when N_2O_3 is dissolved in alkalies (c) Metal nitrates may be reduced by other metals	(a) $N_2O_3 + H_2O \rightarrow 2HNO_2$ (b) $2NaOH + N_2O_3 \rightarrow 2NaNO_2 + H_2O$ (c) $NaNO_3 + Pb$ $\downarrow$ $NaNO_2 + PbO$ $\downarrow$ water crystals of $NaNO_2$	(a) weak acid ($K_A \sim 10^{-6}$) (b) reducing property : $2KMnO_4 + 5NaNO_2 + 3H_2SO_4 \rightarrow K_2SO_4 + + 2MnSO_4 + 5NaNO_3 + 3H_2O$; $HNO_2 + Br_2 + H_2O \rightarrow HNO_3 + 2HBr$ (c) oxidising property : $FeCl_2 + HNO_2 + HCl \rightarrow FeCl_3 + NO + H_2O$; $2SnCl_2 + 2HNO_2 + 4HCl \rightarrow 2SnCl_4 + N_2O + 3H_2O$ $SO_2 + 2HNO_3 \rightarrow H_2SO_4 + 2NO$ (d) not very stable in	

Table 19.2. (continued)

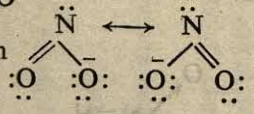
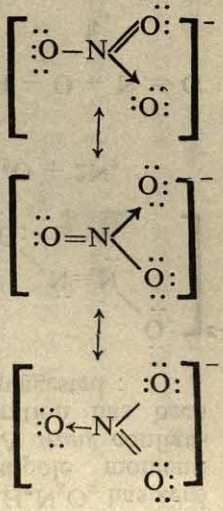
Acid and Formula	Preparative Procedure	Chemical Reactions during preparative procedure	Properties	Structure
			solution : $3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$ (e) reacts with ammonium salts to give nitrogen : $NH_4Cl + HNO_2 \rightarrow N_2 + 2H_2O + HCl$	
Nitric Acid (HNO_3)	(a) Laboratory method (b) Chile saltpetre ($NaNO_3$) method (c) Oxidation of atmospheric nitrogen (Birkeland and Eyde process)	(a) $2KNO_3 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_3$ (b) Chile saltpetre is heated with conc.H_2SO_4 in iron retorts ; $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$ cooled in silica tubes to get conc. HNO_3. (c) $N_2 + O_2 \rightleftharpoons 2NO$ ($\triangle H = +43$ KCals ; endothermic) There is no change in volume in this reaction. The reaction, being endothermic, is carried out at ~ 3000°C under electric arc. The NO formed is cooled as rapidly as possible. This is then led into oxidation chambers where it is converted to NO_2 : $2NO + O_2 \rightarrow 2\ NO_2$; It is then treated with water and more O_2 in several absorption towers filled wtih quartz pieces $4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$	(a) It is a strong acid ; (b) The nature of its reactions with metals depends on their position in the electrochemical series. Those metals, which are above hydrogen in the electrochemical series, can liberate H_2 from HNO_3 but the nascent hydrogen also reduces HNO_3 to NO_2, N_2O etc : $Zn + 4HNO_3(conc) \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$ $4Zn + 10HNO_3(dil.) \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$ Those elements placed below hydrogen in the electrochemical series cannot liberate H_2. They are oxidised by HNO_3 and air to nitrates and NO is	

Table 19.2. (continued)

Acid and Formula	Preparative Procedure	Chemical Reactions during preparative procedures	Properties	Structure
		However this method is not in much use now because of high cost of production	given off : $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$	
	(d) Ammonia Oxidation (Ostwald process)	Ammonia does not easily react with air or oxygen — even if it reacts the product is N_2 : $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$ But when NH_3 and air are mixed in the ratio 1 : 7 and then led through heated platinum gauge catalyst NO is produced : $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ The NO is cooled rapidly and mixed with fresh oxygen when NO_2 is produced. Finally NO_2 is led through water under pressure to get aqueous HNO_3 : $4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$	However H_2 is liberated when the metal concerned is placed well above hydrogen in the spectro-chemical seiries : $Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2$ The acid does not react with gold and platinum because of their inertness. These two dissolve in aqua regia(HCl : HNO_3 = 3:1) because of the presence of some Cl_2 and NOCl. (c) It is a strong oxidant : $C + 4HNO_3 \rightarrow CO_2 + 4NO_2 + 2H_2O$ $S + 2HNO_3 \rightarrow H_2SO_4 + 2NO$ $3I_2 + 10HNO_3 \rightarrow 6HIO_3 + 10NO + 2H_2O$ $6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$. $3H_2S + 2HNO_3 \rightarrow 3S + 4H_2O + 2NO$ (d) HNO_3 is used in nitration of organic compounds : $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$	

Pure ammonia and air in the ratio 1 : 8 are mixed and the mixture is allowed to move up through catalyst chambers (Fig. 19.3). The catalyst consists of several racks of platinum wire gauze maintained at 700°C. The reaction is exothermic and hence after a while no heat supply is necessary to maintain the temperature. Since the gaseous mixture comes in contact with several racks of platinum wire gauze catalyst conversion to NO is almost 90%. The issuing gas is rapidly cooled to about 200°C when it reacts with more oxygen to give NO_2. The NO_2 gas is led through the bottom of absorption towers made of granite and filled with quartz pieces. From the top water is sprayed into the absorption towers. Thus under the counter current principle NO_2 moves up while water moves down. The following reactions take place :

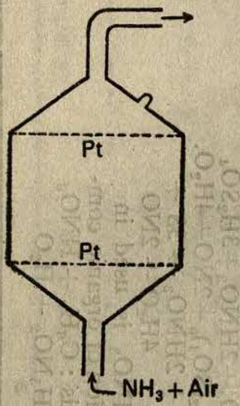


Fig. 19.3. Platinum gauze catalyst chamber

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

The HNO_2 decomposes to form NO and HNO_3 :

$$3HNO_3 \rightarrow 2NO + HNO_3 + H_2O$$

This NO is again reacted with oxygen and more HNO_3 is produced.

Sometimes the gaseous mixture of NO and O_2 is led through sodium carbonate or lime whereby mixtures of nitrite and nitrate is obtained :

$$Na_2CO_3 + 2NO + O_2 \rightarrow NaNO_3 + NaNO_2 + CO_2$$

$$2Ca(OH)_2 + 4NO + 2O_2 \rightarrow Ca(NO_3)_2 + Ca(NO_2)_2 + 2H_2O$$

Calcium salts are used as fertiliser.

19.9. NITROGEN HALIDES

Only two halides, namely NF_3 and NCl_3, are known. On electrolysis of fused ammonium bifluoride (NH_4HF_2) in a copper vessel complex reactions take place. A number of gases HF, N_2, N_2O, O_2, O_3, NH_2F, NHF_2 and NF_3 are obtained. The gaseous mixture is first led over a bed of KF and MnO_2 and the issuing gas is solidified by cooling. Ultimately NF_3(B.P. 119°C) is separated from the accompanying products by fractional distillation. This is a very stable compound and is not readily hydrolysed.

NCl_3 is obtained by the oxidation of NH_4Cl by chlorine in the presence of little acid. A liquid (B.P. $\sim$ 70°C) is thereby obtained :

$$NH_4Cl + 3Cl_2 \rightarrow NCl_3 + 4HCl$$

This is an explosive compound and is hydrolysed to ammonia and hypochlorous acid :

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HClO$$

In contrast to NF_3, NCl_3 is readily hydrolysed because of the fact that H_2O molecules can make a nucleophilic attack on the chlorine atoms which possess *d* orbitals. Note fluorine has no *d* orbitals.

19.10. BINARY NITRIDES

The type of classification proposed for the binary hydrides and binary carbides is also applicable to the binary nitrides. Based on the type of bonding we find the following three types : (a) ionic nitrides (b) covalent nitrides and (c) transition metal nitrides.

I. Ionic Nitrides : Those metals whose ionisation potentials are quite low and whose reduction potentials are quite negative give these ionic type nitrides. Examples are the nitrides of the alkalies and the alkaline earths : Li_3N, Na_3N, K_3N, Mg_3N_2 etc. Of these Li_3N and Mg_3N_2 are formed by the reaction of these metals with nitrogen at ordinary temperature. The ionic nitrides are easily hydrolysed :

$$Li_3N + 3H_2O \rightarrow 3LiOH + 3NH_3$$

The ionic radius of the nitride ion is 1.71A.

II. Covalent Hydrides : These nitrides are formed by the elements of groups IIIB, IVB, VB, VIB and VIIB. Covalent bonding forces operate between nitrogen and the second element. Their properties are comparable to those usually shown by covalent compounds. Examples are NCl_3, NF_3, BN, NO etc. Nitrides of hydrogen NH_3, N_2H_4 are also covalent. Boron nitride is like graphite. The bonds are covalent but the compound forms a planar giant molecule. Unlike covalent compounds boron nitride is very hard and has a high melting point.

III. Transition Metal Nitrides : These are formed as a result of penetration of nitrogen into the interstices of the crystal lattice of transition metals. Usual rules of combining power do not hold here. Melting points of these nitrides are very high. These nitrides are commonly prepared by reacting the transition metals with nitrogen at elevated temperature :

Nitride :	TiN	ZrN	VN	TaN
M.P.°(C) :	2947	2982	2300	3087

19.11. PREPARATION OF NITROGEN

Air is an abundant source of nitrogen. The boiling points of nitrogen and oxygen are – 196°C and – 183°C. Thus on fractional distillation of liquid air nitrogen will come out earlier than oxygen. Nitrogen thus obtained is admixed with oxygen and little argon. The oxygen is removed either (a) by reacting with hydrogen over a heated platinum catalyst or (b) by passing the gas over heated copper. Small quantities of pure nitrogen can be obtained in the laboratory by heating ammonium nitrite :

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

The water produced can be easily removed by some dehydrating agent like P_4O_{10}.

In the elementary state nitrogen is quite inert.

19.12. HYDRIDES OF PHOSPHORUS

Phosphours has two hydrides : PH_3 and P_2H_4. Their properties are like those of covalent compounds.

19.12.1. Phosphine : This hydride can be prepared by a number of methods:

1. Elementary phosphorus and elementary hydrogen react at about 300°C to form PH_3.

2. Calcium phosphide, Ca_3P_2, is formed when phosphorus vapour is passed over hot quicklime, CaO. Hydrolysis of this phosphide gives PH_3 :

$$Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$$

3. PH_3 is also obtained by heating white phosphours with NaOH solution. The reaction is usually carried out in a flask provided with an inlet tube and a delivery tube. The air inside the flask is flushed out by a stream of coal gas or hydrogen. The evolved PH_3 is collected over water. PH_3 is admixed with a small amount of diphosphine, P_2H_4, which is readily inflammable. This explains why flashes are seen and white rings of smoke are observed when PH_3 comes out of water. The white rings are due to fine particles of P_4O_{10}.

$$4P + 6H_2O \rightarrow PH_3 + 3H_3PO_2$$

$$4P + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$$

Properties : It is a colourless gas but gives out a fishy odour. Its aqueous solution is neutral. Compared to ammonia it is a weaker electron donor. Unlike ammonia it does not form complex compounds. It is a reducing agent:

$$3AgNO_3 + PH_3 \rightarrow Ag_3P + 3HNO_3$$

$$Ag_3P.3AgNO_3 + 3H_2O \rightarrow 6Ag + 3HNO_3 + H_3PO_3$$

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$$

Phosphine reacts with dry hydrogen halides to give phosphonium halides :

$$PH_3 + HI \rightarrow PH_4I$$

Phosphonium halides are readily hydrolysed by water :

$$PH_4I + H_2O \rightarrow PH_3 + I^- + H_3O^+$$

Structure : Its structure is parallel to that of NH_3. Phosphorus is tetrahedral and sp^3 hybridised. There are three covalent bonds between phosphorus and the three hydrogen atoms. The fourth sp^3 hybrid orbital is occupied by a lone pair of electrons.

19.12.2. Diphosphine : This hydride is obtained alongwith phosphine. There is no alternative, independent method. The phosphine gas is cooled when a yellow liquid (B.P. 52°C) is obtained first. This yellow liquid is the diphosphine. On further cooling phosphine (B.P. −87°C) is obtained as a liquid. Diphosphine is unstable to heat :

$$3P_2H_4 \rightarrow 2P + 4PH_3$$

Diphosphine is also a reducing agent. Its structure is parallel to that of N_2H_4 in that each phosphorus is connected to two hydrogens and one phosphorus while there is a lone pair of electrons left on each phosphorus.

19.13. OXIDES OF PHOSPHORUS

The two important oxides of phosphorus are $P_2O_3(P_4O_6)$ and $P_2O_5(P_4O_{10})$. Some of the important characteristics of these two oxides are given below :

Oxidation number	$+3$	$+5$
Formula	$P_2O_3(P_4O_6)$	$P_2O_5(P_4O_{10})$
Melting Point (°C)	24	350 (sublimes)
Reaction with water	H_3PO_3 (phosphorous acid)	H_3PO_4 (phosphoric acid)

$\longrightarrow$

acidic properties increase/reducing properties decrease

19.13.1. Phosphorous Oxide : Phosphorous oxide $P_2O_3(P_4O_6)$ alongwith small amount of phosphoric oxide $P_2O_5(P_4O_{10})$ is formed when a mixture of oxygen and nitrogen (as a diluent) in the ratio 3 : 1 is passed over white phosphorus at about 50°C. A glass wool plug is used at the mouth of the delivery tube when P_2O_5 (P_4O_{10}) is retained but the lower oxide comes out. It is waxy in nature. It slowly dissolves in water to give phosphorous acid :

$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$

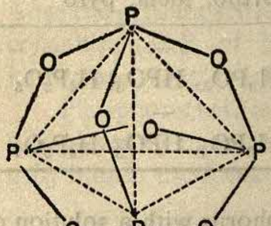


Fig. 19.4
Structure of P_4O_6

Structure: Molecular weight determination shows that it is a tetrameric molecule. Vapour density also points to the same molecular weight. Four phosphorus atoms are sitting at the four corners of a tetrahedron. Each pair of phosphorus atoms is bridged by an oxygen atom (Fig. 19.4).

19.13.2. Phosphoric Oxide : This higher oxide of phosphorus is obtained when white phosphorus is burnt in an excess of air. It is purified by sublimation at about 35°C in a stream of oxygen. It is well known as a dehydrating agent. It reacts with water to form H_3PO_4 :

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

It can extract water from H_2SO_4 and HNO_3 to give the corresponding anhydrides SO_3 and N_2O_5 :

$$2H_2SO_4+P_4O_{10} \rightarrow 2SO_3+4HPO_3 \text{ ; } 4HNO_3+P_4O_{10} \rightarrow 2N_2O_5+4HPO_3$$

Structure : When we compare P_4O_{10} with P_4O_6 we find that the former higher oxide has four more oxygen atoms. These four oxygen atoms are linked one each to the four phopsphorus atoms via double bonds. This will explain the formal valence five of each phosphorus atom. The four phosphorus atoms are situated at the four corners of a tetrahedron. Each pair of phosphorus atoms is bridged by an oxygen atom. Finally each phosphorus has an additional oxygen linked by a double bond. In support of the tetrameric structure we have good vapour density value and molecular weight (Fig. 19.5).

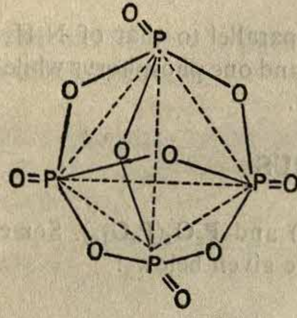


Fig 19.5. Srructure of P_4O_{10}

19.14. OXYACIDS OF PHOSPHORUS

There are too many oxyacids of phosphorus. But only a selection of the comparatively simpler ones is presented in Table 19.3.

Table 19.3. Some Typical Oxyacids of Phosphorus

Oxidation Number	Formula and Name	Ortho, meta, pyro
+1	H_3PO_2(hypophosphorous acid)	—
+3	H_3PO_3(phosphorous acid)	H_3PO_3, HPO_3, $H_4P_2O_5$
+4	$H_4P_2O_6$(hypophosphoric acid)	—
+5	H_3PO_4(phosphoric acid)	H_3PO_4, HPO_3, $H_4P_2O_7$

19.14.1. Hypophosphorous Acid : On boiling white phosphorus with a solution of NaOH sodium hypophosphite is obtained. On treating the solution with barium hydroxide sparingly soluble barium hypophosphite is precipitated. On treating this barium salt with dilute H_2SO_4 barium sulphate is precipitated and the acid is retained in solution. On crystallisation the free acid H_3PO_2(M.P. 27°C) is obtained :

$$P_4 + 3H_2O + 3NaOH \rightarrow PH_3 + 3NaH_2PO_2$$
$$Ba(H_2PO_2)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_3PO_2$$

This is a weak monobasic acid ($K_A \sim 10^{-2}$). This is a good reducing agent. It is oxidised in air :

$$H_3PO_2 + 4AgNO_3 + 2H_2O \rightarrow 4Ag + H_3PO_4 + 4HNO_3$$
$$3H_3PO_2 + 2CuSO_4 + 3H_2O \rightarrow 2CuH + 3H_3PO_3 + 2H_2SO_4$$
$$H_3PO_2 + O_2 \rightarrow H_3PO_4$$

19.14.2. Phosphorous Acid : White phosphorus is kept in molten state under water and then chlorine is led through. Thus phosphorous acid is produced in solution :

$$2P + 3Cl_2 \rightarrow 2PCl_3 \ ; \ PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

It is a weak dibasic acid ($K_A{}^I \sim 10^{-2}$). It is a weaker reducing agent than H_3PO_2. The meta- and pyro-forms of this acid are obtained by controlled dehydration of H_3PO_3 :

$$\begin{tikzcd}
\underset{\text{(ortho)}}{2H_3PO_3} \arrow[r, "\text{little heat}", "-H_2O"'] & \underset{\text{(pyro)}}{H_4P_2O_5} \arrow[d, "\text{strong heat}", "(-H_2O)"'] \\
H_3PO_3 \arrow[r, "\text{strong heat}", "-H_2O"'] & \underset{\text{(meta)}}{HPO_2}
\end{tikzcd}$$

19.14.3. Phosphoric Acid : On dissolving P_4O_{10} in water phosphoric acid is produced :

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

In industrial scale preparation of this acid crushed phosphate rock or crushed bone (basically calcium phosphate) is used as the raw material. This is reacted with sulphuric acid under mechanical stirring :

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3CaSO_4.2H_2O$$

After the gypsum settles down the mixture is filtered and the filtrate is allowed to crystallise (M.P. of H_3PO_4, ~ 43°C). Aqueous solution of H_3PO_4 (85%) is known as *syrupy phosphoric acid* as the solution attains a syrupy consistency.

Phosphoric acid is a weak tribasic acid. However all the three hydrogens can be replaced by metal ions to give monoacid, diacid and normal salts. Controlled dehydration produces pyro- and metaphosphoric acid :

$$\underset{\text{(ortho)}}{H_3PO_4} \xrightarrow{\text{little heat}} \underset{\text{(pyro)}}{H_4P_2O_7} \xrightarrow{\text{strong heat}} \underset{\text{(meta)}}{HPO_3}$$

Structures of the Acids : The structures of the more important phosphorus oxyacids are shown in Fig. 19.6.

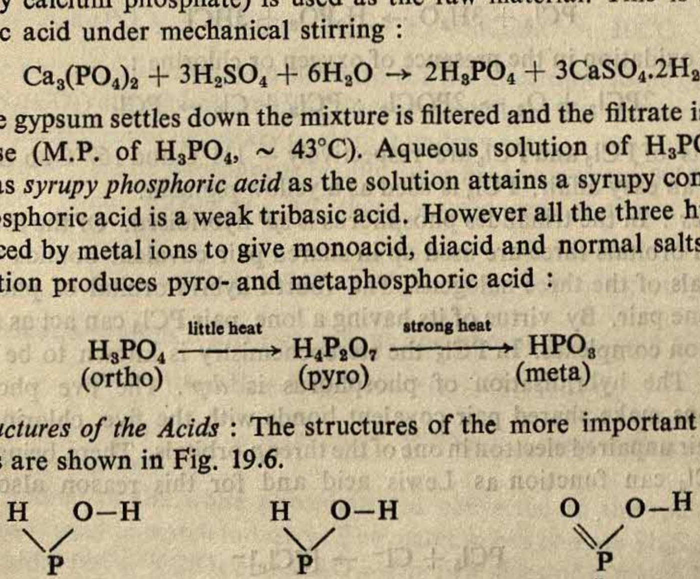


Fig. 19.6. Structures of phosphorus oxyacids

Note that in H_3PO_2, H_3PO_3 and H_3PO_4 there are one, two and three – OH groups. The hydrogens of the – OH groups alone are replaceable by metal ions. The phosphorus — oxygen bonds alone are polar, the oxygen end being more negative than the phosphorus end. Concentration of electron density on the oxygen makes the hydrogen attached to it more dissociable. Hence H_3PO_2, H_3PO_3 and H_3PO_4 are monobasic, dibasic and tribasic acids respectively. Also note that there is no electronegativity difference between phosphorus and hydrogen (both having a value 2.1) and hence the bonds are perfectly covalent and these hydrogens are not replaceable by metal inos. However H_3PO_4 being tribasic, it does not follow that it cannot give other than normal salts. In fact it does.

19.15. HALIDES OF PHOSPHORUS

The halides are of two types : trihalides and pentahalides. These halides (PF_3, PCl_3, PBr_3, PCl_5 etc.) are monomeric in nature.

The syntheses of the trihalides are accomplished by reacting halogens with excess of white phosphorus. In the synthesis of PCl_3 dry white phosphorus is taken in retort. There is a chlorine inlet tube that runs into the retort and positioned slightly above the layer of the white phosphorus. The inlet tube is so adjusted that it is neither too close to nor too far above the phosphorus. This helps to control the reaction properly. The retort is placed on a sand bath. The evolved PCl_3 contains little PCl_5. The issuing gas is cooled and the impurity PCl_5 is removed. PCl_3 is hydrolysed by water :

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

It undergoes oxidation in the presence of oxygen or chlorine :

$$2PCl_3 + O_2 \rightarrow 2POCl_3 \ ; \ PCl_3 + Cl_2 \rightarrow PCl_5$$

Melting points of PCl_3 and PCl_5 are respectively − 111°C and 167°C so that their separation is an easy affair. PCl_5 is used as a yellow pigment.

Structures : In the trihalides phosphorus is sp^3 hybridised. Of the four tetrahedral hybrid orbitals three are used up in shared pair covalent bounds with the three *p* orbitals of the three halogens. The fourth hybrid orbital of phosphorus carries the lone pair. By virtue of its having a lone pair PCl_3 can act as a donor in coordination complexes. In PCl_5 the stereochemistry is known to be trigonal bipyramidal. The hybridisation of phosphorus is dsp^3. The five phosphorus outer electrons make shared pair covalent bonds with the five chlorine atoms which use their unpaired electron in one of the three *p* orbitals. There being unused *d* orbitals PCl_5 can function as Lewis acid and for this reason also suffers hydrolysis :

$$PCl_5 + Cl^- \rightarrow [PCl_6]^-$$

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl \ ; \ POCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

19.17. PREPARATION OF PHOSPHORUS

Phosphorus occurs in nature in several forms : phosphorite, $Ca_3(PO_4)_2$; Fluoro apatite, $3Ca_3(PO_4)_2.CaF_2$; chloro apatite, $3Ca_3(PO_4).CaCl_2$ etc. Most of these minerals are converted to superphosphate of lime for use as fertiliser (Chapter 16). Only a small amount is recovered as elementary phosphorus.

Industrial scale preparation of phosphorus involves reaction of phosphorite rock, silica and coke in an electric furnace at about 3200°C. The lower part of the furnace is provided with two electrodes between which an arc is set up to reach the desired high temperature (Fig. 19.7). At this high temperature white phosphorus vapourises and comes out through a side outlet near the top of the furnace. The vapour is cooled in cold water and is processed in the form of sticks and stored under water. The slag, calcium silicate, is drawn out through a side hole near the bottom of the furnace. The mixture of phosphorite rock, silica and coke is fed into the furnace through the top.

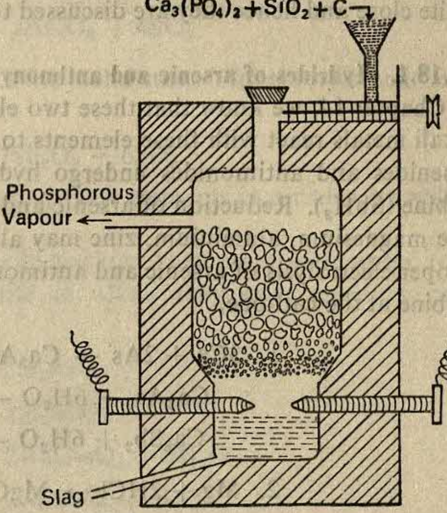


Fig. 19.7
Industrial preparation of white phosphorus

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow P_4 + 6CaSiO_3 + 10CO$$

White phosphorus is transformed into the red allotropic form on heating in an inert (N_2/CO_2) atmosphere at 250°C for several hours. The red variety is stable in air and hence it is not necessary to store it under water.

Properties : White phosphorus readily takes fire in air above 30°C and burns with a green flame. P_4O_6/P_4O_{10} are thereby produced. It reacts readily with halogens, sulphur, etc :

$$2P + 3Cl_2 \rightarrow 2PCl_3 \; ; \; PCl_3 + Cl_2 \rightarrow PCl_5; \; 2P + 5S \rightarrow P_2S_5$$

In strong alkali solutions it gives phosphine and phosphorous acid :

$$4P + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$

Comparatively red phosphorus is far inert. It does not react with air or alkalies like the white phosphorus.

Uses : Most of the white phosphorus is converted to the red form. Red phosphorus is used in match industry. The match sticks contain Sb_2S_3, alongwith an oxidant like PbO_2, $KClO_3$ or K_2CrO_4. The two sides of a match box carry a layer of gum, an abrasive (eg. powdered glass) and red phosphorus. On striking the match stick against the side of the match box there is a momentary flash which lights the match stick head.

Phosphor bronze alloy is made of copper (79 – 90%), tin (25 – 10%) alongwith small amount of phosphorus.

19.18. ARSENIC AND ANTIMONY

In group VB these two elements are the two metalloids. Their chemistry is quite close and hence they are discussed together in the following sections.

19.18.1. Hydrides of arsenic and antimony : From the general discussion we had in Chapter 14, we know that these two elements produce covalent hydrides. The alkali metals react with these elements to give arsenides and antimonides. These arsenides and antimonides undergo hydrolysis and furnish arsine (AsH_3) and stibine (SbH_3). Reduction of arsenic and antimony salts by strongly basic metals like magnesium, aluminium, zinc may also be used to get the desired hydrides. Proper electrolysis of arsenic and antimony compounds may also give arsine and stibine at the cathode.

1. $3Ca + 2As \rightarrow Ca_3As_2$

$$Ca_3As_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2AsH_3$$

$$Ca_3Sb_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2SbH_3$$

2. $Mg + 2HCl \rightarrow MgCl_2 + 2H$(nascent hydrogen)

$$As_2O_3 + 12H \rightarrow 2AsH_3 + 3H_2O$$

$$Sb_2O_3 + 12H \rightarrow 2SbH_3 + 3H_2O$$

The boiling points of AsH_3 and SbH_3 are − 55°C and − 17°C respectively. The two hydrides can be purified by liquefaction and fractional distillation from any accompanying impurities. These hydrides, as we have mentioned earlier, are less stable than NH_3 and PH_3 but more reducing in character :

$$AsH_3 + 6AgNO_3 + 3H_2O \rightarrow 6Ag + 6HNO_3 + H_3AsO_3$$

$$SbH_3 + 6AgNO_3 + 3H_2O \rightarrow 6Ag + 6HNO_3 + H_3SbO_3$$

These hydrides are easily decomposed by heat and give shining mirrors of the respective elements. This property is made use of in the detection of arsenic. The test is known as Marsh's test. When arsenic compound is heated with Zn + HCl the nascent hydrogen liberated produces AsH_3. The evolved gas is passed through a heated tube when the hydride breaks down to hydrogen and a mirror of elementary arsenic is formed :

$$2AsH_3 \rightarrow 2As + 3H_2$$

Stibine also gives a similar reaction.

·19.18.2 Oxides of Arsenic and Antimony : At the very beginning of this Chapter we have mentioned that these elements are known to exhibit two different oxidation numbers + 3 and + 5 in their chemistry because of the inertness of the s^2 pair of electrons in their + 3 state. The oxides of these two metalloid elements also show two types : $As_2O_3(As_4O_6)$, $Sb_2O_3\,(Sb_4O_6)$ and $As_2O_5(As_4O_{10})$, $Sb_2O_5(Sb_4O_{10})$. These oxides have several similarities with the oxides of phosphorus.

Arsenious oxide, $As_2O_3(As_4O_{10})$, is obtained in the gaseous state on heating arsenical pyrites FeAsS or cobaltite CoAsS :

$$2FeAsS + 5O_2 \rightarrow Fe_2O_3 + As_2O_3 + 2SO_2$$

$$4CoAsS + 9O_2 \rightarrow 4CoO + 2As_2O_3 + 4SO_2$$

The evolved gas on cooling gives As_2O_3 in the solid state. Similar treatment of antimony ores provides antimony oxides :

$$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2$$

One can however easily guess that on heating these elements in air also we will get the desired oxides.

These trivalent oxides are amphoteric in nature. They react with water to give arsenious or antimonous acids while in alkali they give arsenites or antimonites :

$$As_2O_3 + 3H_2O \rightarrow 2H_3AsO_3$$

$$Sb_2O_3 + 3H_2O \rightarrow 2H_3SbO_3$$

$$As_2O_3 + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2O$$

$$Sb_2O_3 + 2NaOH \rightarrow \underset{\text{(metaantimonite)}}{2NaSbO_2} + H_2O$$

With HCl they expectedly give $AsCl_3$ and $SbCl_3$.

These oxides cannot be easily oxidised in air to their higher oxides. The lower oxides are oxidised by HNO_3 and the resulting higher oxyacids are heated to get the higher oxides :

$$\begin{array}{l} 2AsO_3 + 4HNO_3 + H_2O \rightarrow 2H_3AsO_4 + 4NO_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{heat} \\ \qquad\qquad\qquad\qquad\qquad\quad As_2O_5 + 3H_2O \end{array}$$

$$\begin{array}{l} Sb_2O_3 + 4HNO_3 + H_2O \rightarrow 2H_3SbO_4 + 4NO_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{heat} \\ \qquad\qquad\qquad\qquad\qquad\quad Sb_2O_5 + 3H_2O \end{array}$$

According to general rules the lower oxides are expected to be reductants while the higher oxides are oxidants (see next section)

Structures : Vapour density and molecular weight measurements indicate that the oxides are tetrameric i.e. the real compositions are As_4O_6, As_4O_{10}, Sb_4O_6 and Sb_4O_{10}. It can be followed that their structures are parallel to those of the corresponding phosphorus oxides (Fig. 19.4 and 19.5).

19.18.3. Oxyacids of Arsenic and Antimony : These two elements have two different types of oxides. Therefore their oxyacids are also of two different types. It is not possible to get all the oxyacids in the solid crystalline state. But there is no doubt that they do exist in solution. Salts of their oxyacids are well known.

Sodium arsenite is obtained by the dissolution of As_2O_3 in NaOH:

$$As_2O_3 + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2O$$

Sodium arsenite is a good reducing agent :

$$Na_3AsO_3 + I_2 + H_2O \rightarrow Na_3AsO_4 + 2HI$$

$$Na_3AsO_3 + 2FeCl_3 + H_2O \rightarrow Na_3AsO_4 + 2FeCl_2 + 2HCl$$

Arsenic acid is commonly obtained by boiling As_2O_3 in HNO_3 and then crystallising :

$$As_2O_3 + 4HNO_3 + H_2O \rightarrow 2H_3AsO_4 + 4NO_2$$

$$\downarrow \text{ concentration}$$

$$H_3AsO_4.\tfrac{1}{2}H_2O \text{ crystals}$$

Arsenic acid is an oxidant and liberates iodine from acidified KI :

$$H_3AsO_4 + 2KI + 2HCl \rightarrow H_3AsO_3 + I_2 + H_2O + 2KCl$$

Antimonous oxide $Sb_2O_3(Sb_4O_6)$ reacts with alkali hydroxide to give antimonite salts. But there is a difference in the compositions of antimonites and arsenites. The arsenites have the tetrahedral $[AsO_4]^{3-}$ while the antimonites have the octahedral $[Sb(OH)_6]^-$ units.

$$Sb_2O_3 + 4HNO_3 \rightarrow Sb_2O_5 + 4NO_2 + 2H_2O$$

$$Sb_2O_5 + 2NaOH + 5H_2O \rightarrow 2Na[Sb(OH)_6]$$

19.18.4. Halides of Arsenic and Antimony : For both the elements we have both the trihalides and the pentahalides. It is a general experience that as we move from fluorine to iodine the tendency towards forming the pentahalides decreases. This evidently is due to the reducing ability of the higher halide ion, particularly of the iodide. The following halides are known :

AsF_3	$AsCl_3$	$AsBr_3$	AsI_3
AsF_5	—	—	—
SbF_3	$SbCl_3$	$SbBr_3$	SbI_3
SbF_5	$SbCl_5$	—	—

The formation of the pentafluorides is definitely facilitated by the very high electronegativity and also very small size of the fluorine atom.

The above halides are prepared by following different procedures :

$$2As + 3Cl_2 \rightarrow 2AsCl_3 \text{ (liquid)}$$

$$As_2O_3 + 3CaF_2 + 3H_2SO_4 \rightarrow 2AsF_3 + 3CaSO_4 + 3H_2O$$

$$2As + 5F_2 \rightarrow 2AsF_5 + \text{some liquid } AsF_3$$

$$2As + 3Br_2 \text{ (in } CS_2 \text{ solution)} \rightarrow 2AsBr_3$$

$$Sb_2O_3 + 6HF \rightarrow 2SbF_3 + 3H_2O$$

$$SbCl_3 + Cl_2 \rightarrow SbCl_5$$

These halides are readily hydrolysed :

$$AsCl_3 + 3H_2O \rightarrow H_3AsO_3 + 3HCl$$

$$\begin{array}{l} SbCl_3 + H_2O \rightarrow SbOCl + 2HCl \\ \qquad\qquad\qquad\quad \downarrow H_2O\ \text{(heat)} \\ \qquad\qquad\qquad\quad Sb_2O_3 + HCl \end{array}$$

$$2SbCl_5 + 5H_2O \rightarrow Sb_2O_5 + 10HCl$$

19.18.5. Preparations of Arsenic and Antimony : The common ores of arsenic are : arsenical pyrites (mispickel) FeAsS ; nickel glance, NiAsS ; realgar, As_2S_3. Commonly the ore (mostly FeAsS) is taken in an earthenware retort. The retort has an iron tube that goes almost half way down into the retort. On heating arsenic sublimes and condenses inside the iron tube :

$$FeAsS \rightarrow FeS + As$$

Alternatively FeAsS is heated in air to get As_2O_3 which is then mixed with coke and heated again. The volatile arsenic is allowed to condense on the inside surface of an inverted funnel :

$$\begin{array}{l} 2FeAsS + 5O_2 \rightarrow Fe_2O_3 + As_2O_3 + 2SO_2 \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow + 3C \\ \qquad\qquad\qquad\qquad\qquad\quad 2As + 3CO \end{array}$$

Antimony occurs in nature mostly in the form of stibnite Sb_2S_3. The ore is first fused and then mixed with powdered iron and again heated. Iron is removed as the slag FeS. Fused antimony collects under the fused FeS :

$$Sb_2S_3 + 3Fe \rightarrow 3FeS + 2Sb$$

$$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2$$

$$Sb_2O_3 + 3CO \rightarrow 2Sb + 3CO_2$$

Properties : It has been pointed out in section 19.3 that arsenic and antimony form graphite like planar macromolecular structure with sp^2 hybridisation of their orbitals. However when their vapours are rapidly cooled different tetrameric As_4 and Sb_4 structures are formed. Vapour density supports the tetrameric formulation. In this form they resemble P_4 tetrameric units.

These elements react with air to form the trioxides As_2O_3/Sb_2O_3. With halogens they produce, depending on reaction conditions, either the trihalides or the pentahalide. The elements are oxidised to the pentavalent oxyacids by nitric acid :

$$As + 5HNO_3 \rightarrow H_3AsO_4 + 5NO_2 + H_2O$$

Uses : Arsenic is used in some forms of bronzes. Presence of arsenic adds to the lustre, strength and hardness of the alloys. Due to its poisonous nature it is sometimes used as insecticide in soils during cultivation. Antimony is also used alongwith the lead strips in lead batteries to add stability to the plates. This alloy of lead and antimony is not easily destroyed by the H_2SO_4 of the lead battery. Type metal is an alloy of lead (70—85%) and antimony (30—15%).

19.19. BISMUTH

Among the elements of this group bismuth is the most metallic. Its electronegativity is the lowest and so also is the trend of ionisation potential.

19.19.1. Hydride of Bismuth : Bismuthine, the bismuth hydride, (BiH_3) is quite unstable and readily decomposes. A mixture of powdered bismuth and magnesium on being treated with dilute acids gives a mixture of hydrogen and bismuthine. Bismuthine gas also responds to Marsh's test i.e. bismuthine breaks up while passing through a heated tube to give a shining mirror of metallic bismuth.

19.19.2. Oxides of Bismuth : Two oxides of trivalent bismuth (Bi_2O_3) and pentavalent bismuth (Bi_2O_5) are known. On burning metallic bismuth in air yellow coloured Bi_2O_3 is produced :

$$4Bi + 3O_2 \rightarrow 2Bi_2O_3$$

Thermal decomposition of bismuth oxynitrate (also called subnitrate) $BiONO_3$ also gives Bi_2O_3 :

$$4BiONO_3 \rightarrow 2Bi_2O_3 + 4NO_2 + O_2$$

This lower valent oxide is basic in character and hence reacts with acids to give trivalent bismuth salts :

$$Bi_2O_3 + \text{acids} \rightarrow \text{bismuth (III) salts (like } BiCl_3,\ Bi_2(SO_4)_3 \text{ etc.)}$$

It is however difficult to get the higher oxide, Bi_2O_5 in pure state.

19.19.3. Oxyacids of Bismuth: For both arsenic and antimony the lower oxyacids, namely arsenious acid and antimonous acid are known. But the corresponding lower oxyacid of bismuth is not known. This is an indication that the lower oxide of bismuth, Bi_2O_3, is wholly basic. But the higher oxyacid is known as sodium salt. Fusion of a mixture of Bi_2O_3 and NaOH gives brown coloured $NaBiO_3$. Heating together of Bi_2O_3 and Na_2O_2 also produces $NaBiO_3$. However it has not been possible to obtain this compound in a pure state. Nonetheless sodium bismuthate is a very useful oxidant. It oxidises manganese (II) in the presence of H_2SO_4/HNO_3 to the violet permanganate. The sodium bismuthate being insoluble in water can be easily removed by filtration. The permanganate so produced can be titrated by a standard ferrous ammonium sulphate solution and the amount of manganese evaluated :

$$2Mn(NO_3)_2 + 5NaBiO_3 + 16HNO_3 \rightarrow 2HMnO_4 + 5Bi(NO_3)_3 + 5NaNO_3 + 7H_2O$$

19.19.4. Bismuth Nitrate and Subnitrate : Bi_2O_3 is dissolved in dilute HNO_3, the solution concentrated and then cooled to get crystals of $Bi(NO_3)_3.5H_2O$. In large excess of water (in the absence of HNO_3) the salt undergoes hydrolysis to give bismuth subnitrate :

$$Bi(NO_3)_3 + H_2O \rightarrow BiO(NO_3) + 2HNO_3$$

In the presence of large amount of water other salts of bismuth (III) also undergo hydrolysis to give precipitates of oxysalts :

$$BiCl_3 \xrightarrow{HCl} \text{no precipitate} \; ; \; BiCl_3 \xrightarrow[\text{water}]{\text{excess}} BiOCl \text{ precipitate}$$

19.19.5. Halides of Bismuth : BiF_3, BiF_5, $BiCl_3$, $BiBr_3$ and BiI_3 are known. The compounds are obtained by following common procedures:

$$Bi_2O_3 + 6HF \rightarrow 2BiF_3 + 3H_2O$$

$$2Bi + 3F_2 \rightarrow 2BiF_3 \xrightarrow[600°C]{F_2} BiF_5$$

The increase of metallic properties in bismuth is proved from an inspection of the properties of BiF_3. This compound shows typical properties of ionic compound. It is not decomposed even at red heat.

19.19.6. Preparation of Bismuth : The major ores of bismuth are bismuth ochre (Bi_2O_3), bismuth glance (Bi_2S_3) and bismuth carbonate $(BiO)_2CO_3$. These ores are first roasted in air to get Bi_2O_3 which is then reduced by coke :

$$2Bi_2S_3 + 9O_2 \rightarrow 2Bi_2O_3 + 6SO_2$$

$$(BiO)_2CO_3 \rightarrow Bi_2O_3 + CO_2$$

$$Bi_2O_3 + 3C \rightarrow 2Bi + 3CO$$

The impure bismuth is then reacted with HNO_3 to get $Bi(NO_3)_3$. This nitrate is next thermally decomposed to get pure Bi_2O_3. This is then again reacted with coke to obtain pure bismuth.

Uses : Bismuth is used to obtain alloys of low melting points.

Wood metal : Bi 50%, Pb 25%, Sn, 12.5%, Cd 12.5% (M.P. 71°C)

Rose metal : Bi 50%, Pb 25%, Sn 25%

These alloys find use in electric fuse wire, fire alarm wire etc.

EXERCISES

1. Present a comparative study of the hydrides of nitrogen and phosphorus.
2. Classify the nitrides and give an account of their properties and nature of the bonding.
3. Discuss the two major allotropes of phosphorus.
4. Present a comparative account of the chemistry of the group VB of the periodic table.
5. How do you justify that arsenic and antimony are very close in their chemistry?
6. Write short notes on :
   (*a*) active nitrogen (*b*) hydrazine (*c*) hydrazoic acid (*d*) sodium bismuthate (*e*) Marsh's test (*f*) oxides of phosphorus
7. Write an essay on the oxyacids of nitrogen.

8. Discuss the structures of the following :
   (*a*) hydrazoic acid (*b*) ammonia (*c*) hypophosphorous acid (*d*) hydroxylamine (*e*) nitric acid and nitrate ion
9. Give a comparative account of the three important oxyacids of phosphorus
10. Describe the chemistry involved in the industrial preparation of the following chemicals :
    (*a*) ammonia (*b*) ammonium sulphate from gypsum (*c*) white phosphorus (*d*) nitric acid (*e*) phosphoric acid (*f*) hydrazine sulphate (*g*) superphosphate of lime
11. Complete the following reactions :
    (*a*) $CaC_2 + N_2 \rightarrow$
    (*b*) $P + H_2O \rightarrow$
    (*c*) $FeCl_3 + NH_2OH \rightarrow$
    (*d*) $Ca_3(PO_4)_2 + SiO_2 + C \rightarrow$
    (*e*) $NH_3 + NaOCl \rightarrow$
    (*f*) $As_2O_3 + HNO_3 + H_2O \rightarrow$
    (*g*) $H_3PO_2 + AgNO_3 + H_2O \rightarrow$
    (*h*) $H_3AsO_4 + KI + HCl \rightarrow$

CHAPTER 20

GROUP VIB. MAINLY OXYGEN AND SULPHUR

20.1. INTRODUCTION

This group VIB consists of the elements oxygen, sulphur, selenium, tellurium and polonium. By virtue of their position in the periodic table all these elements contain s^2p^4 outer shell configuration. This group is closer to the seventh group and hence their electronegativities are even higher than the corresponding members of the preceding group VB of the periodic table. We shall make first a comparative study of the chemistry of these elements. This discussion will be followed by a resume of the chemistry of the two elements oxygen and sulphur. The last mentioned element polonium is a radioactive element and was discovered by Becquerel and the Curies at the fag end of the nineteenth century (Chapter 2).

20.2. A COMPARATIVE STUDY OF THE CHEMISTRY OF THE GROUP VIB ELEMENTS

Physical Properties : 1. All the members of this group possess the same outer electronic configuration : s^2p^4. These elements are thus just two electrons short of the following noble gases.

2. Since these elements are members of group VIB it is only natural to assume that their chemistry will be dominated by hexavalence. It is true that this is the maximum valence that sulphur and the later elements can exhibit but not oxygen. If oxygen is to show hexavalence it has to expand its valence shell to twelve — which it cannot because it has no *d* orbitals. The valence shell of oxygen is limited to only eight. The result is obvious. It cannot show a valence beyond two. Other elements can show valences two, four and six. This becomes possible for the later elements because of their having *d* levels.

3. The ionisation potentials of these elements (Table 20.1) are rather high and quite close to the respective preceding members of group VB. These elements therefore can never form cations.

4. These elements are closest to the halogens. Hence their electronegativities are very high (cf : oxygen, 3.5 ; fluorine, 4.0 ; sulphur, 2.5, chlorine, 3.0)

5. There are two ways these elements can attain the valence two. The first way is via acquiring two electrons from some electropositive elements (forming binegative ions like O^{2-}, S^{2-}) and the second is by sharing electrons with other elements (as in H_2O, H_2S).

Chemical Properties : 1. The elements of this group all form covalent hydrides. Due to strong hydrogen bonding effect H_2O is a liquid. In the other elements electronegativities fall and hence the hydrogen bonding gets weaker. Thus H_2S and the binary hydrides are gaseous in nature. With increasing atomic number the sizes of the atoms increase resulting in a greater distance between hydrogen and the hydride forming element. This results in weakening of the bond and a consequent increase in the acidity of the hydrides of the heavier members :

Hydride	H_2O	H_2S	H_2Se
K_A^1	1×10^{-14}	1×10^{-7}	1.7×10^{-4}

2. Because of the relatively high electronegativity the oxides of these elements are acidic in nature (eg. SO_2, SO_3, SeO_3 etc). The acid character of the oxyacids increases with increasing oxidation number of the central element :

Acid Character :	H_2SO_3	<	H_2SO_4 ;	H_2SeO_3	<	H_2SeO_4
Oxidation Number :	$+4$		$+6$	$+4$		$+6$

On the other hand acidity gradually decreases with increasing atomic number provided the oxidation number remains the same.

3. It has already been mentioned that oxygen cannot expand its valence shell beyond eight and hence it cannot form more than two covalent bonds. Thus we see that Cl_2O, F_2O exist with oxygen but with sulphur compounds like SF_4, SF_6 etc. are found.

Table 20.1. A Comparative Study of the Group VIB Elements

Element	Atomic Number	Electron Distribution	Ionisation Potential (*ev*)	Atomic Radius (A)	Electro-negativity	M.P. (°C)
O	8	$[He]2s^22p^4$	13.6 35.11 54.89 77.39	0.66	3.5	-219
S	16	$[Ne]3s^23p^4$	10.36 23.40 35.00 47.29 72.50	1.04	2.5	12.8* 119**
Se	34	$[Ar]3d^{10}4s^24p^4$	9.75 21.50 32.00 42.00 68.30	1.17	2.4	217
Te	52	$[Kr]4d^{10}5s^25p^4$	9.01 18.60 31.00 38.60	1.37	2.1	450
Po	84	$[Xe]4f^{14}5d^{10}6s^26p^4$	8.43	1.64	.....	254

*rhombic sulphur ; **monoclinic sulphur

20.3. ALLOTROPY

Allotropic forms of oxygen and sulphur have already been discussed in Chapter 10. The usual oxygen is diatomic molecular O_2. The other form, namely ozone, is the triatomic O_3. Sulphur has a large number of allotropic forms of which rhombic and monoclinic forms are the most important. Both these forms are octatomic S_8. Similarly selenium also exists in rhombic and monoclinic forms and both these are Se_8. These forms are crystallised from CS_2 solution below 72°C.

20.4. BINARY OXIDES

These are compounds of oxygen with a second element. Several classifications of binary oxides have been proposed from time to time. The one based on acid/base character and nature of the molecular form is presented in Table 20.2. The salient properties of these binary oxides are given below :

1. *Normal Oxide* : These are the oxides in which the oxidation number of oxygen is the usual -2. These oxides again may be classified in three categories : (*a*) basic oxides (*b*) amphoteric oxides and (*c*) neutral oxides. The basic oxides are given by those elements whose ionisation potentials are quite low and whose reduction potentials are quite negative. The alkalies and the alkaline earths form such oxides. Aqueous solution of such basic oxides give alkaline reaction due to OH^- ion. These oxides give salts when neutralised with acids :

$$Na_2O + H_2O \rightarrow 2NaOH \quad ; \quad Na_2O + 2HCl \rightarrow 2NaCl + H_2O$$

A few elements like aluminium, beryllium, zinc give amphoteric oxide. These react with both acids and bases :

$$Al_2O_3 + 6HCl \rightarrow AlCl_3 + 3H_2O \qquad \text{. . . basic character}$$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O \qquad \text{. . . acid character}$$

Those oxides which show none of the basic or acidic characters are obviously the neutral oxides. Examples of this class are H_2O, CO, NO.

2. *Peroxides* : These are salts of hydrogen peroxide H_2O_2. In these compounds there is an $[O-O]^{2-}$ single covalent bond in the peroxide ion. On reaction with acids they liberate H_2O_2. Peroxides usually act as oxidants. In presence of acids they also react as reductants towards strong oxidising agents like $KMnO_4$:

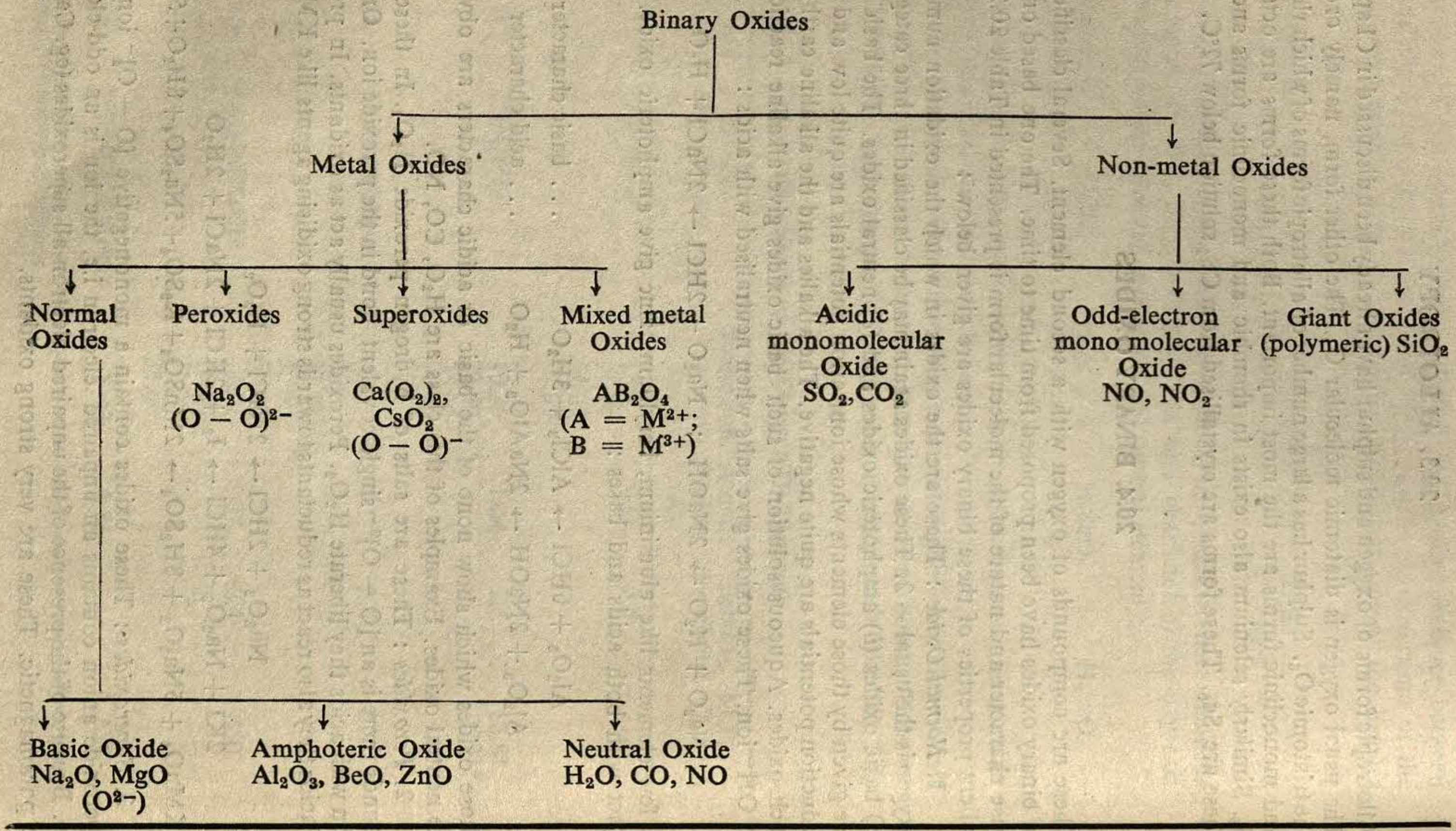
$$Na_2O_2 + 2HCl \rightarrow 2NaCl + H_2O_2$$

$$2KI + Na_2O_2 + 4HCl \rightarrow I_2 + 2KCl + 2NaCl + 2H_2O$$

$$2KMnO_4 + 5Na_2O_2 + 8H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 5Na_2SO_4 + 8H_2O + 5O_2$$

3. *Superoxides* : These oxides contain a mononegative $[O-O]^-$ ion. The superoxide anion contains an unpaired electron i.e. the ion is an odd-electron ion. Because of the presence of the unpaired electron all superoxides (eg. $Ca(O_2)_2$) are paramagnetic. These are very strong oxidants.

Table 20.2. Classification of Binary Oxides



4. *Mixed Metal Oxides* : Spinels are mixed oxides containing two trivalent metals and one bivalent metal. Typical examples are :

$$MgFe_2O_4,\ Co_3O_4\ (CoO.Co_2O_3),\ Fe_3O_4\ (FeOFe_2O_3)\ \text{etc.}$$

5. *Non-metal Oxides* : (*a*) In most cases these oxides are monomeric and acidic in nature. Common examples are SO_2, SO_3, CO_2 etc.

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

Most of these oxides are formed by electronegative non-metals.

(*b*) *Odd electron non-metal Oxides*: There are a limited few non-metal oxides which carry odd electrons in their molecules. These are usually monomeric and paramagnetic in nature. Examples are found in NO, NO_2, ClO_2.

(*c*) *Polymeric non-metal oxides* : One such example is found in silica which is polymeric through oxygen bridging. These oxides have high melting points. Structure is depicted in Fig. 18.4.

20.5. HYDRIDES OF OXYGEN

There are two hydrides of oxygen : H_2O and H_2O_2. Detailed discussion on water is uncalled for. The only point that we would like to make out is its hydrogen bonding ability which leads to association and thus to its liquid state.

Hydrogen Peroxide : This very useful commercial product is usually obtained by three different methods ;

1. *By reaction of metal peroxides with acids* : Hydrated barium peroxide, $BaO_2.8H_2O$, is mixed with water to make a thick slurry and then cooled down to 0°C. This slurry is treated with a mixture of dilute H_2SO_4 and little HCl also maintained at 0°C. On treating the peroxide slurry with small amounts of the acid at a time hydrogen peroxide is formed :

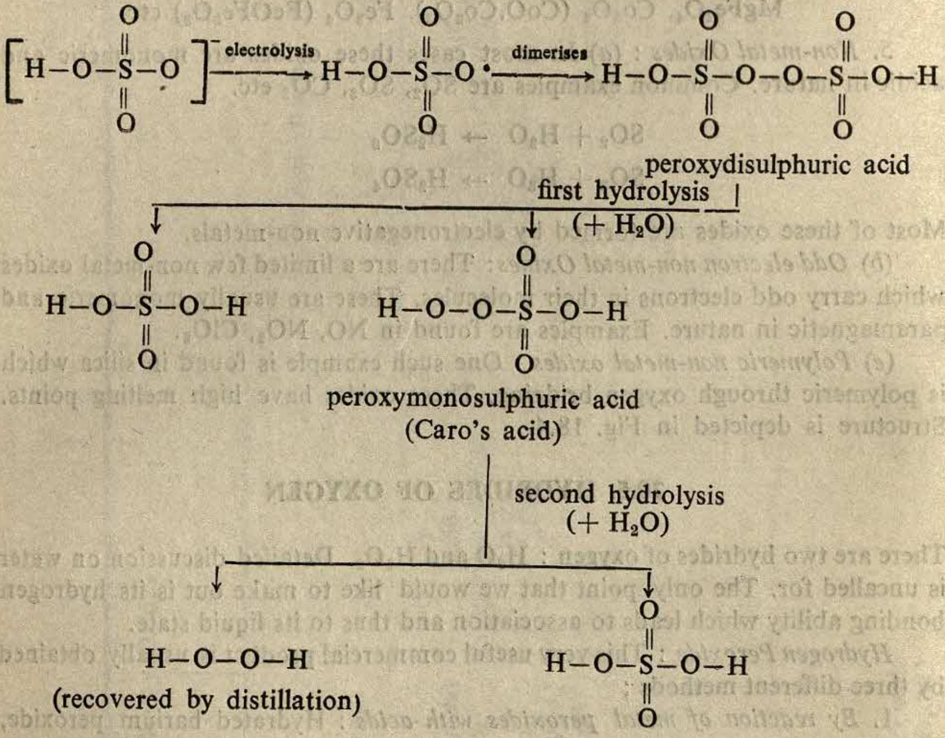
$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$

On filtering off the insoluble $BaSO_4$ the filtrate contains 15-20% H_2O_2. Several variations of this method are in vogue. For example, $BaO_2.8H_2O$ is often replaced by Na_2O_2. Sometimes the above H_2SO_4/HCl mixture is replaced by a stream of CO_2 gas. The resulting insoluble $BaCO_3$ is next filtered off and the filtrate carries the H_2O_2 in aqueous solution.

2. *Electrolytic procedure* : On electrolysis of 50% H_2SO_4 in the cold good amount of peroxydisulphuric acid is produced in the anode chamber. Hydrolysis of this acid gives finally H_2O_2.

at the anode : $2HSO_4^- \rightarrow H_2S_2O_8 + 2e$
at the cathode : $2H^+ + 2e \rightarrow H_2$
hydrolysis : $H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4$
$\downarrow H_2O$
$H_2O_2 + H_2SO_4$

Oxidation and eventual dimerisation of the bisulphate radical and subsequent hydrolysis of the peroxydisulphuric acid are shown in the scheme given below :



Electrolysis of a mixture of K_2SO_4 and H_2SO_4 gives at the anode crystals of colourless potassium peroxydisulphate $K_2S_2O_8$. The crystals of $K_2S_2O_8$ may be treated with aq.H_2SO_4 and then distilled under reduced pressure to get H_2O_2 :

$$H_2S_2O_8 + 2H_2O \rightarrow H_2O_2 + 2H_2SO_4$$

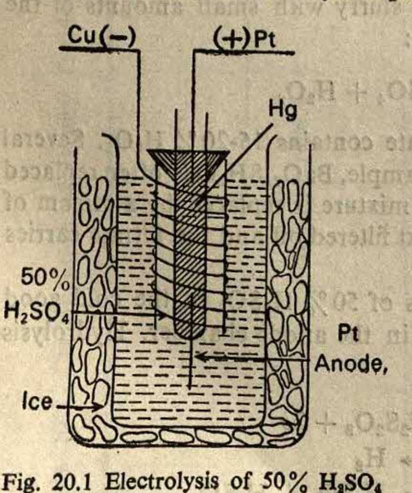


Fig. 20.1 Electrolysis of 50% H_2SO_4

The electrolytic procedure of obtaining $H_2S_2O_8$ has been shown in Fig. 20.1. A thin platinum wire is sealed to a glass tube which contains mercury for establishing electrical contact. The platinum wire serves as the anode. The tube carrying the platinum anode is enclosed into another tube of wider bore. This outer tube is open at its lower end and is wrapped on the outside by a copper wire. The copper wire serves as the cathode. The whole set-up is lowered into a solution of 50% H_2SO_4 taken in a beaker. This beaker is cooled by crushed ice. The outer open tube, which surrounds the tube carrying the platinum wire, acts as a diaphragm.

3. *Synthesis via anthraquinol* A 10% solution of 2-ethyl anthraquinol is prepared in benzene and some higher alcohol. This solution is oxidised by oxygen to 2-ethylanthraquinone while oxygen is reduced to H_2O_2. The 2-ethylanthraquinone is reduced by hydrogen in presence of palladium catalyst to 2-ethylanthraquinol and reused (Fig. 20.2).

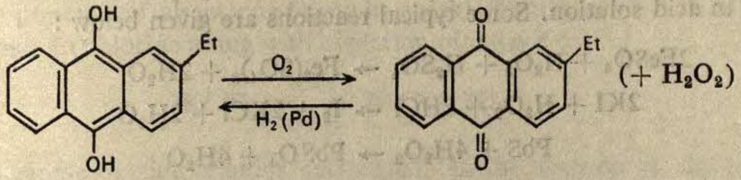


Fig. 20.2. Oxidation of 2-ethylanthraquinol by oxygen and synthesis of H_2O_2

Concentration and isolation of H_2O_2 : All the three methods described above give us a solution of hydrogen peroxide. The solution is distilled under reduced pressure to get rid of the major amount of water. The remaining amount of concentrated solution is again distlled carefully under further reduced pressure to get nearly 99% H_2O_2. On cooling down to about − 10°C crystals of H_2O_2 (M.P. − 0.89°C) may be obtained. The hydrogen peroxide available commercially is in the form of aqueous solution. The concentration of H_2O_2 is expressed in terms of the oxygen that will be available on heating the solution :

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

10 volume of H_2O_2 means a solution of hydrogen peroxide which wll liberate ten times its own volume of oxygen on heating. Note that at N.T.P. 34 gram of H_2O_2 (M.W. of H_2O_2 = 34) will give $\frac{1}{2} \times 22.4$ litres of oxygen. 1 gm. H_2O_2 will give 329.4 ml. of oxygen. We can calculate that 1% H_2O_2 will give 3.294 times of its own volume of oxygen. According to such estimate 10 volume of H_2O_2 is 3.04% H_2O_2. 100 volume of H_2O_2 is therefore 30% in strength. This concentrated solution of hydrogen peroxide is called *perhydrol.* In the presence of slight preservatives like glycerol, alcohol or H_2SO_4 hydrogen peroxide remains stabilised for long time.

Properties of Hydrogen Peroxide : Hydrogen Peroxide exhibits three distinct classes of properties : (*a*) acid properties (*b*) oxidising properties and (*c*) reducing properties.

1. *Acid Properties* : H_2O_2 is a weak dibasic acid :

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \quad ; \quad K_A^1 \sim 2.5 \times 10^{-12}$$

It is a slightly stronger acid than water ($K_W \sim 10^{-14}$). The second dissociation will be even weaker than the first. Normally reactions with alkalies give normal peroxides like Na_2O_2, BaO_2 etc. However an acid salt, namely a hydroperoxide, is obtained on reacting sodium peroxide with an alcoholic solution of sodium ethoxide :

$$Na_2O_2 + EtOH \rightarrow NaOOH + NaOEt$$

2. *Oxidising Properties* : Hydrogen peroxide shows strong oxidising properties in acid and alkali solutions :

$$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O \quad ; \quad E^\circ = 1.77 \text{ volts}$$
$$HO_2^- + H_2O + 2e \rightleftharpoons 3OH^- \quad ; \quad E^\circ = 0.87 \text{ volts}$$

The positive values and their magnitudes tell us that H_2O_2 will behave as a strong oxidant in acid solution. Some typical reactions are given below :

$$2FeSO_4 + H_2O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2H_2O$$
$$2KI + H_2O_2 + 2HCl \rightarrow I_2 + 2KCl + 2H_2O$$
$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

3. *Reducing Properties* : Hydrogen peroxide behaves as a reducing agent towards some very powerful oxidants like permanganate, chlorine :

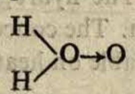
$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$$
$$Cl_2 + H_2O_2 \rightarrow 2Cl + O_2$$

With acidified dichromate hydrogen peroxide gives the blue perchromic oxide :

$$H_2Cr_2O_7 + 4H_2O_2 \rightarrow 2CrO_5 + 5H_2O$$

Structure of H_2O_2 : We can write two possible structures for this compound :

H−O−O−H ;



(a) (b)

We have earlier observed that hydrogen peroxide is a weak dibasic acid. It should therefore have two hydroxyl −OH groups in the molecule. It does give salts like Na_2O_2. Besides, it reacts with diethyl sulphate to give diethyl peroxide, which can be reduced by zinc and acetic acid to furnish ethyl alcohol :

$$\begin{array}{c} HO - OH + (C_2H_5)_2SO_4 \rightarrow C_2H_5 - O - O - C_2H_5 + H_2SO_4 \\ \qquad\qquad\qquad\qquad \downarrow + 2H \\ \qquad\qquad\qquad\qquad 2C_2H_5OH \end{array}$$

This reaction also supports the first structure (*a*). If the structure were the second one i.e. (*b*) we would have got ether instead of the alcohol. In all the reduction reactions of H_2O_2 oxygen is liberated. Hydrogen peroxide was prepared from oxygen−18 enriched oxygen. Such labeled H_2O_2 was used in some reduction reactions and the liberated oxygen was found to be enriched in O − 18. These experiments indicate that H_2O_2 carries the −O−O− linkage and that this linkage remains unaltered during reduction. Structure 20.3 gives an idea of the currently known structure of the compound. The two − OH groups lie in two planes which are at an angle of about 97°.

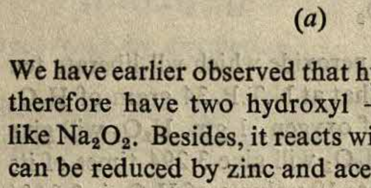


Fig. 20.3. Structure of H_2O_2

Uses of H_2O_2 : It is widely used in the laboratory as a reagent, in the cleaning of garments, and as antibacterial.

20.6. PREPARATION OF OXYGEN

20.6.1. Laboratory Methods : 1. Commonly potassium chlorate is heated to about 250°C in presence of about one-fourth its weight of MnO_2 catalyst. The chlorate decomposes to chloride along with evolution of oxygen :

$$2KClO_3 \xrightarrow[250°C]{Mno_2} 2KCl + 3O_2$$

The manganese dioxide remains unchanged. In the absence of the MnO_2 the chlorate, on heating, goes over to perchlorate and chloride :

$$4KClO_3 \xrightarrow{360°C} 3KClO_4 + KCl$$

On heating further the perchlorate decomposes at about 600°C to give KCl and oxygen. Manganese dioxide inhibits these undesirable reactions and forces the potassium chlorate to decompose to give directly potassium chloride and oxygen. It is believed that MnO_2 reacts with $KClO_3$ to form an intermediate Mn_2O_7 which then decomposes to oxygen and MnO_2 :

$$\begin{array}{l} KClO_3 + 2MnO_2 \rightarrow KCl + \underset{\displaystyle 2MnO_2 + 1\tfrac{1}{2}O_2}{\underset{\downarrow}{Mn_2O_7}} \end{array}$$

2. Alkali peroxides are decomposed by water to produce oxygen :

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

3. H_2O_2 is decomposed in the presence of MnO_2 to give oxygen :

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

4. Some metal oxides are thermally decomposed to give oxygen :

$$2HgO \rightarrow 2Hg + O_2 \quad ; \quad 2Ag_2O \rightarrow 4Ag + O_2$$

5. Electrolysis of acidulated or alkaline water gives oxygen at the anode :

$$\begin{array}{rl} & H_2O \rightleftharpoons H^+ + OH^- \\ \textit{at the cathode}: & 2H^+ + 2e \rightarrow H_2 \\ \textit{at the anode}: & 2OH^- \rightarrow H_2O + \tfrac{1}{2}O_2 + 2e \end{array}$$

20.6.2. Industrial Preparation : Huge quantities of oxygen are obtained via liquefaction of air. Ordinary air is liquefied under high pressure and low temperature. Thereafter fractional distillation of the liquid air is resorted to, to separate oxygen (B.P. − 183°C) from nitrogen (B.P. − 196°C). Nitrogen, having a comparatively lower boiling point, comes out in the earlier fraction while much of the oxygen is retained. The remaining oxygen is refractionated to get a reasonably pure variety. Oxygen gas is stored in steel cylinders under high pressure (~ 2000 lb/sq. inch).

Properties : Oxygen is a diatomic gas. Apparently it might seem that all the electrons are paired, particularly because of our way of writing the structure of O_2 with a double bond between the two atoms. In reality every diatomic molecule of oxygen has two unpaired electrons as has been ascertained from the determination of the magnetic susceptibility and hence the magnetic moment. The paramagnetic behaviour has been successfully explained on the basis of the molecular orbital theory (Chapter 10).

Oxygen gas is a good oxidant. On heating it reacts with many elements to give their oxides :

$$C + O_2 \rightarrow CO_2 \quad ; \quad S + O_2 \rightarrow SO_2$$

In the presence or absence of catalysts oxygen reacts with many non-metal oxides and hydrides to give higher oxides of industrial importance :

$$2NO + O_2 \rightarrow 2NO_2 \quad ; \quad 2SO_2 + O_2 \rightarrow 2SO_3$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

Uses : Oxygen is indispensable in combustion, in breathing and other metabolic reactions. Oxygen is in common use in oxy-acetylene torch for welding of metals. It is also used in oxy-hydrogen blowpipe. It is a must for trouble free breathing for divers and mountain climbers and high altitude flying people. It is in every day use in hospitals.

20.7. OZONE

It is an allotropic modification of oxygen. It is triatomic oxygen. It is usually prepared from oxygen via silent electric discharge. The conversion reaction is endothermic :

$$3O_2 \rightleftharpoons 2O_3 - 68.4 \text{ KCal (endothermic)}$$

Ozone can be obtained from oxygen around 3000°C but the very hot oxygen has to be removed as quickly as possible otherwise much of the ozone formed undergoes decomposition back to oxygen. However a mixture of ozone and oxygen is usually obtained by the passage of silent electric discharge through oxygen. Two different types of apparatus are used for the purpose.

Siemens' Ozoniser : The apparatus consists of two horizontal concentric glass tubes. The inner tube is open at one end through which passes an electrical

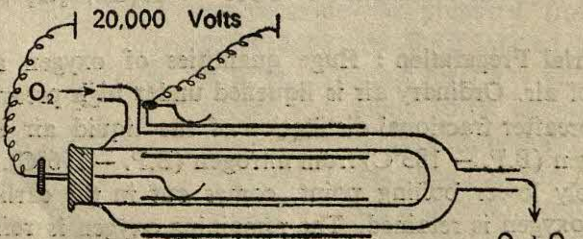


Fig. 20.4 Siemens' ozoniser

contact terminal. The outer tube has an inlet for oxygen and an outlet for the mixture of oxygen and ozone at the lower end. The outside of the outer tube and the inside of the inner tube are lined with tin foil. The foils act as the electrodes and a voltage of 20,000 is maintained. A slow stream of oxygen is passed through the annular space. Care is taken to avoid sparking as the heat generated may decompose the ozone. The issuing gas is a mixture of oxygen and ozone. On cooling down to − 193°C ozone condenses to a blue solid.

Brodie's Ozoniser: The essential feature of this apparatus is again two concentric tubes making up a narrow annular space. The mouth of the inner tube carries a conducting wire. The outer tube has an inlet for oxygen. The lower end of this outer tube is bent upwards into a thin tube which serves as the exit for the mixture of ozone and oxygen. This whole set-up is lowered vertically into a solution of dilute sulphuric acid. The inner tube is also filled with dilute sulphuric acid. Another conducting wire is lowered into the sulphuric acid in which the apparatus is immersed. On applying a very high potential difference between the electrodes and on passing a slow stream of oxygen through the annular space a mixture of ozone and oxygen is produced.

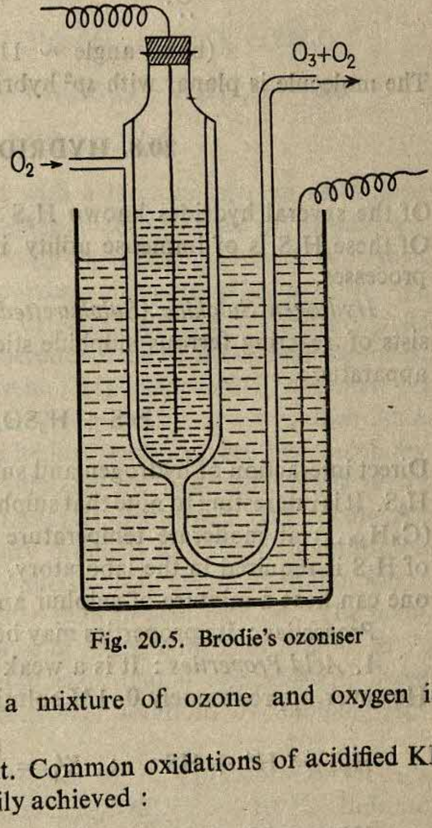


Fig. 20.5. Brodie's ozoniser

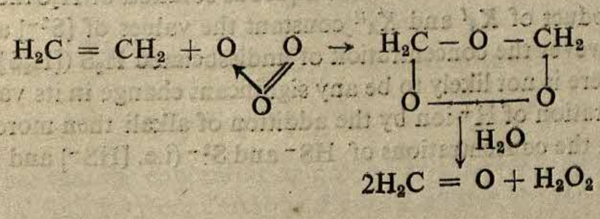
Properties : Ozone is a strong oxidant. Common oxidations of acidified KI to I_2, PbS to $PbSO_4$, $SnCl_2$ to $SnCl_4$ are easily achieved :

$$2KI + H_2O + O_3 \rightarrow I_2 + 2KOH + O_2$$

$$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$$

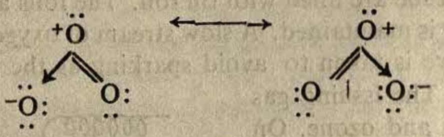
$$3SnCl_2 + 6HCl + O_3 \rightarrow 3SnCl_4 + 3H_2O$$

It can also bring about many oxidations of organic compounds, : particularly hydrocarbons to aldehydes via the formation of ozonides followed by hydrolysis :



$$H_2C=CH_2 + \underset{O}{O\quad O} \rightarrow \begin{array}{c} H_2C-O-CH_2 \\ |\qquad\qquad| \\ O\text{———}O \end{array} \xrightarrow{H_2O} 2H_2C=O + H_2O_2$$

Structure of ozone : The structure of this allotropic form of oxygen has been described in Chapter 10. The two resonance forms are depicted below :



(bond angle ~ 117° ; O–O = 1.28A)

The molecule is planar with sp^2 hybridised oxygen.

20.8. HYDRIDES OF SULPHUR

Of the several hydrides known H_2S and H_2S_2 are the two important ones. Of these H_2S is of immense utility in the laboratory and in many industrial processes.

Hydrogen Sulphide (*Sulphuretted Hydrogen*) : The laboratory method consists of reacting ferrous sulphide sticks in dilute HCl or H_2SO_4 in a Kipp's apparatus :

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$$

Direct interaction of hydrogen and sulphur at elevated temperature also produces H_2S. It is interesting to note that sulphur can dehydrogenate paraffin hydrocarbons (C_nH_{2n+2}) at moderate temperature to give H_2S. In fact when small quantity of H_2S is required in the laboratory, for example in semi-micro level detections, one can heat a mixture of sulphur and paraffin to get H_2S.

Properties : Its properties may be discussed under the following four heads:

1. *Acid Properties* : It is a weak dibasic acid. Its solubility in water is low. However approximately 0. 1M solution can be made.

$$H_2S \rightleftharpoons H^+ + HS^- \quad ; \quad K_A^I = \frac{[H^+]\ [HS^-]}{[H_2S]} = \sim 10^{-7}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \quad ; \quad K_A^{II} = \frac{[H^+]\ [S^{2-}]}{[HS^-]} = \sim 10^{-15}$$

In a saturated solution of H_2S in water $[H_2S] \sim 0.\ 1M$. Reactions of other ions with H_2S in aqueous solution will proceed in such a manner that the concentrations of the different species i.e. $[H^+]$, $[HS^-]$, $[S^{2-}]$ and $[H_2S]$ maintain the values of $K_A{}^I$ and $K_A{}^{II}$. Also to be noted is the fact that the product of the two equilibrium constants is around $\sim 10^{-22}$. It therefore follows that if concentration of H^+ ion ($[H^+]$) is increased in a saturated aqueous solution of H_2S then in order to maintain the product of $K_A{}^I$ and $K_A{}^{II}$ constant the values of $[S^{2-}]$ and $[HS^-]$ must decrease. However the concentration of undissociated H_2S ($[H_2S]$) is rather high (0.1M) and there is not likely to be any significant change in its value. If we reduce the concentration of H^+ ion by the addition of alkali then more H_2S will go into solution i.e. the concentrations of HS^- and S^{2-} (i.e. $[HS^-]$ and $[S^{2-}]$) will increase.

2. *Reducing Properties* : The following reactions identify H_2S as a reducing agent. Note that in all the reactions elementary sulphur is precipitated :

$$H_2S + Br_2 \rightarrow 2HBr + S \quad ; \qquad H_2S + Cl_2 \rightarrow 2HCl + S$$

$$H_2O_2 + H_2S \rightarrow 2H_2O + S \quad ; \quad 2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S$$

$$5H_2S + 2KMnO_4 + 3H_2SO_4 \rightarrow 5S + 2MnSO_4 + K_2SO_4 + 8H_2O$$

$$3H_2S + 2K_2Cr_2O_7 + 4H_2SO_4 \rightarrow 3S + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

$$H_2S + 2HNO_3 \rightarrow S + 2NO_2 + 2H_2O$$

3. *Precipitation Properties* : H_2S reacts with a large number of metal ions to give precipitates of their insoluble sulphides under specified pH conditions. The precipitation of a metal sulphide occurs only when the concentration product of the relevant ions in solution exceeds the corresponding solubility product. We have seen in Chapter 9 that the qualitative detection scheme of the metal ions has largely been based on the precipitation difference of the various metal sulphides. The sulphides of mercury (II), copper (II), arsenic (III), bismuth (III), cadmium (II) etc are rather quite insoluble i.e. their solubility products are very low. As a result the concentration products of these sulphides readily exceed their solubility products even in acid medium where the sulphide ion concentration is pretty low. On the other hand the sulphides of nickel (II), manganese (II), cobalt (II), zinc (II) have comparatively higher solubility products and their concentration products exceed their respective solubility products only in alkaline solution where the sulphide concentration is obviously higher than in acid medium. The solubility product of HgS is $\sim 10^{-52}$ while those of MnS, NiS, ZnS are $\sim 10^{-13}$, $\sim 10^{-22}$, $\sim 10^{-23}$ respectively. We thus appreciate that it is possible to have selective precipitation of metal sulphides from their solutions by bubbling H_2S under acid or alkaline medium.

Problem 1 : The solubility product of HgS is 10^{-52}. Concentration of H_2S in a saturated solution is $0.1M$ and the product $K_A^I . K_A^{II} = \sim 10^{-22}$. Indicate whether HgS will be precipitated from a $0.01M$ solution of mercury (II) at pH 4.

Hydrogen ion concentration $= [H^+] = 10^{-4}M$

$$K_A^I . K_A^{II} = \frac{[H^+]^2 \, [S^{2-}]}{[H_2S]} = \sim 10^{-22}$$

We assume for simplicity that the $[H_2S] \simeq 0.1M$ at pH 4 although in reality it should be a little less.

$$\text{Thus} \quad \frac{[10^{-4}]^2 \, [S^{2-}]}{0.1} = 10^{-22} \quad ; \quad \text{therefore } [S^{2-}] = 10^{-15}$$

$$[Hg^{2+}] \, [S^{2-}] = 10^{-2} \times 10^{-15} = 10^{-17}$$

Thus we see that the concentration product in solution at pH 4 exceeds solubility product of HgS very comfortably. Hence HgS will be precipitated completely.

Problem 2. Concentration of H_2S is $2.5 \times 10^{-2} M. K_A{}^I$ and $K_A{}^{II}$ of H_2S are respectively 5.7×10^{-8} and 1.2×10^{-15}. Solubility product of FeS is 3.7×10^{-19}. Calculate the pH at which 0.01 *M* ferrous will be precipitated.

$$H_2S \rightleftharpoons H^+ + HS^- \quad ; K_A^I = \frac{[H^+][HS^-]}{[H_2S]} = 5.7 \times 10^{-8}$$

$$K_A^{II} = \frac{[H^+]\ [S^{2-}]}{[HS^-]} = 1.2 \times 10^{-15} \ ; \ K_A^I \, . \, K_A^{II} = \frac{[H^+]^2\ [S^{2-}]}{[H_2S]} \simeq 1.0 \times 10^{-22}$$

In order that there may be precipitation of FeS the concentration product $[Fe^{2+}]$ $[S^{2-}]$ must exceed the solubility product 3.7×10^{-19}.

Then the $[S^{2-}]$ should exceed $\frac{3.7 \times 10^{-19}}{0.01}$ i.e should exceed the value 3.7×10^{-17}

$$\text{Again} \quad \frac{[H^+]^2 \times 3.7 \times 10^{-17}}{2.5 \times 10^{-2}} = 1.0 \times 10^{-22}$$

Therefore $[H^+] = 10^{-4}$ i.e. pH $\simeq 4$

However the above caluclations are quite approximate as the values of $[H_2S]$, $[S^{2-}]$ are not exact.

4. *Syntheses of Polysulphides* : When powdered sulphur is added to an alkaline or ammoniacal solution and the mixture boiled an orange to red coloured solution is obtained. Such solutions contain polysulphides. The compositions of these polysulphides depend on the amount of sulphur and the concentration of the ammonia or the alkali. The common species present in these solutions are the disulphide ($S_2{}^{2-}$), trisulphide ($S_3{}^{2-}$) etc. On careful distillation these polysulphides give the hydrides like H_2S_2, H_2S_4, H_2S_3. On acidification of the polysulphide solution sulphur is precipitated and sulphide ion is retained in solution.

20.9. OXIDES OF SULPHUR

Several oxides of sulphur are known. Three important ones are described below :

Oxidation number :	+2	+4	+6
Oxide :	SO	SO_2	SO_3

$$\xrightarrow[\text{acid character increases}]{\hspace{8cm}}$$

20.9.1. Sulphur Monoxide : This is obtained on the passage of silent electric discharge through sulphur dioxide or through a mixture of sulphur dioxide and sulphur vapour. This is also obtained via reaction of silver metal and thionyl chloride :

$$2SO_2 \rightarrow 2SO + O_2 \quad ; \quad SO_2 + S \rightarrow 2SO$$

$$SOCl_2 + 2Ag \rightarrow SO + 2AgCl$$

This oxide is very unstable and is easily decomposed into SO_2. The structure obviously is S = O. It appears to be an example of an oxide of bivalent sulphur. There is another opinion that SO is really a mixture of S_2O and SO_2.

20.9.2. Sulphur Dioxide : This oxide of sulphur can be had by a variety of methods. Burning of sulphur in air gives SO_2. Sulphides and bisulphites also decompose on addition of acids to give this oxide :

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + SO_2 + H_2O$$

Metallic copper also reacts with hot concentrated H_2SO_4 to liberate SO_2 :

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2$$

Sulphur dioxide is acidic in nature and is truly the anhydride of sulphurous acid :

$$SO_2 + H_2O \rightarrow H_2SO_3$$

This is a good reducing agent as is revealed by the following reactions :

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

$$H_2O_2 + SO_2 \rightarrow SO_3 + H_2O \rightarrow H_2SO_4$$

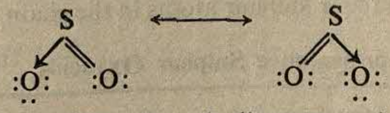
It is quite well known that in the presence of suitable catalysts sulphur dioxide reacts with oxygen to give sulphur trioxide.

Sulphur dioxide also shows oxidising properties in a few limited cases :

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

$$4FeCl_2 + SO_2 + 4HCl \rightarrow 4FeCl_3 + 2H_2O + S$$

Structure : The structure is a resonance hybrid of the forms shown below. The molecule is known to be planar. This means that sulphur uses its sp^2 hybrid orbitals for overlap with suitable orbitals of the two oxygen atoms.



bond angle ~ 120° ; S — O distance ~ 1.45A

Uses : Its major use is in the manufacture of sulphuric acid :

$$SO_2 \xrightarrow[\text{catalyst}]{\text{oxygen+heat}} SO_3 \xrightarrow{H_2O} H_2SO_4$$

It finds use in the laboratory as a reducing agent. It is used in bleaching and as a disinfectant.

20.9.3. Sulphur Trioxide : This oxide, SO_3, is the anhydride of H_2SO_4 :

$$SO_3 + H_2O \rightarrow H_2SO_4$$

In the presence of platinum sponge or vanadium pentoxide (V_2O_5) catalysts. SO_2 reacts very readily with oxygen at moderate temperature to form the trioxide SO_3.

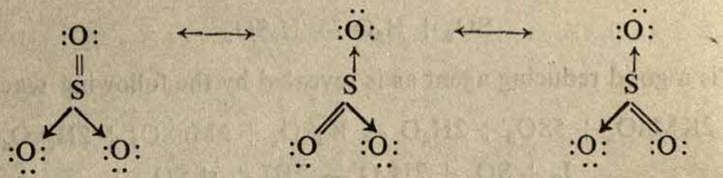
This oxide reacts as expected with metallic oxides to produce metal sulphates :

$$K_2O + SO_3 \rightarrow K_2SO_4 \;;\; CaO + SO_3 \rightarrow CaSO_4$$

It reacts with dry HCl to give chlorosulphonic acid HSO_3Cl :

$$SO_3 + HCl \rightarrow HSO_3Cl \; (SO_2(OH)Cl)$$

Its vapour density 40 tells us that its formula is SO_3. It has no dipole moment. This means that although there is a substantial difference in the electronegativities of the two elements the bond polarities cancel to give a zero resultant for the dipole moment. This is possible only if we accept the following planar resonating forms :



Sulphur uses its sp^2 hybrid orbitals for bonding with the three oxygen atoms. Because of resonance all the sulphur — oxygen distances are the same (1.43A) and the bond angle is 120° as is required for the sp^2 hybridisation of sulphur.

20.10. OXYACIDS OF SULPHUR

Sulphur has a very large number of oxyacids indeed. It is not possible nor is it desirable to give a complete account in this elementary text. In Table 20.3 we present a limited few but important sulphur oxyacids. It is also important to mention that the structures shown in Table 20.3 are not the only possible ones. In fact other structures can also be written. There are more than one opinion on the structure of several of the sulphur oxyacids. Many of the acids exist in solution only although their salts are well characterised. A particularly interesting group of sulphur oxyacids have sulphur-sulphur linkage. These acids are known as *thionic acids* and have two to six sulphur atoms in the chain.

Table 20.3. Some Representative Sulphur Oxyacids

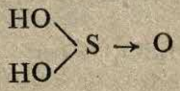
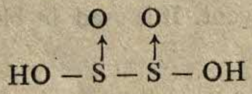
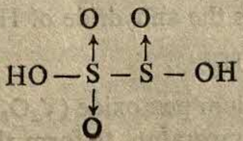
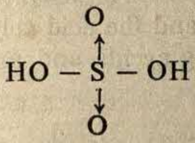
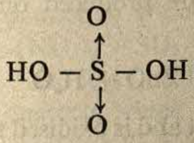
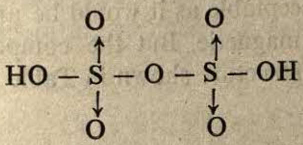
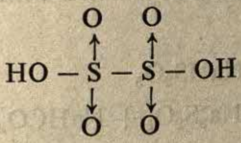
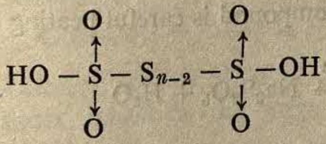
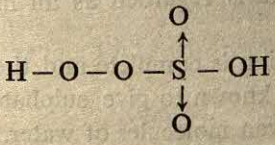
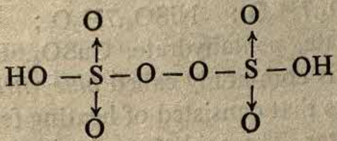
Empirical composition	Structure	Some properties
I. *Oxyacids derived from sulphurous acid*		
H_2SO_3		sulphurous acid ; exists in solution ; salts are known.
$H_2S_2O_4$	 $HO-\overset{\overset{O}{\uparrow}}{S}-\overset{\overset{O}{\uparrow}}{S}-OH$	dithionous (hypo/hydrosulphurous) acid ; exists only in solution ; salts are known.
$H_2S_2O_5$	 $HO-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-\overset{\overset{O}{\uparrow}}{S}-OH$	pyrosulphurous acid ; known only in the form of salts.

Table 20.3. (*Continued*)

Empirical composition	Structure	Some properties
II. *Oxyacids derived from sulphuric acid*		
H_2SO_4	 $\mathrm{HO-}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{-OH}$	sulphuric acid ; acid and salts are well known.
$H_2S_2O_3$	 $\mathrm{HO-}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{-OH}$	thiosulphuric acid ; acid is unstable ; salts are well known.
$H_2S_2O_7$	 $\mathrm{HO-}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{-O-}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{-OH}$	pyrosulphuric acid ; salts can be had on careful manipulation.
III. *Thionic Oxyacids*		
$H_2S_2O_6$	 $\mathrm{HO-}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{-}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{-OH}$	dithionic acid ; known in solution and also in salts.
$H_2S_nO_6$	 $\mathrm{HO-}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{-}S_{n-2}\mathrm{-}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{-OH}$	polythionic acids ; acids are unstable ; salts are known.
IV. *Peroxy acids*		
H_2SO_5	 $\mathrm{H-O-O-}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{-OH}$	peroxymonosulphuric acid ; known only in solution.
$H_2S_2O_8$	 $\mathrm{HO-}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{-O-O-}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{-OH}$	peroxydisulphuric acid and salts are well known.

20.10.1. Sulphurous acid : This acid, H_2SO_3, is produced on dissolution of SO_2 in water. It is a weak dibasic acid : $K_A{}^I$, 1.7×10^{-2} ; $K_A{}^{II}$, 5.6×10^{-8}. Both the normal and the acid salts are known ; eg. Na_2SO_3 and $NaHSO_3$.

Sodium bisulphite is obtained by passing SO_2 gas through a solution of $NaCO_3$. This is also obtained by treating a solution of Na_2SO_3 by SO_2 :

$$Na_2CO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3 + CO_2$$

$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

The normal salt is obtained by passing controlled amount of SO_2 (i.e. not in excess) through a solution of NaOH. Both the normal and the acid sulphites liberate SO_2 on treatment with acids. Both are reducing agents and are oxidised to sulphates.

20.10.2. Dithionous acid and its salts : These are produced on reduction of bisulphites with zinc :

$$2NaHSO_3 + Zn \rightarrow Na_2S_2O_4 + ZnO + H_2O$$

Sodium dithionite is a very powerful reducing agent and is oxidised to the sulphite. The monomeric formula HSO_2 is not acceptable as it would be an odd-electron molecule and therefore should be paramagnetic. But the compound $Na_2S_2O_4$ is known to be diamagnetic. Hence the structure shown in Table 20.3 has been accepted.

20.10.3. Pyrosulphites : The mother acid $H_2S_2O_5$ is not known. The sodium salt may be obtained by reacting sodium bisulphite solution with more sulphur dioxide and then neutralising with Na_2CO_3 :

$$NaHSO_3 + SO_2 \rightarrow NaHS_2O_5$$

$$NaHS_2O_5 + Na_2CO_3 \rightarrow Na_2S_2O_5 + NaHCO_3$$

An alternative way of obtaining the compound is careful heating of $NaHSO_3$:

$$2NaHSO_3 \xrightarrow{\text{heat}} Na_2S_2O_5 + H_2O$$

20.10.4. Sulphuric Acid : This is one of the most important acids used in commerce and industry. The consumption of this acid is regarded as an index of the advancement of a country.

This is a strong acid. The first acid dissociation is complete and the value for the second is $\sim 10^{-2}$. Most of the metals are known to give sulphate salts. Some bivalent metal sulphates crystallise with seven molecules of water. These sulphates are called *vitriols* : $FeSO_4.7H_2O$; $NiSO_4.7H_2O$; $CoSO_4.7H_2O$; $MgSO_4.7H_2O$ etc. But copper sulphate, pentahydrate, $CuSO_4.5H_2O$, is not a true vitriol by definition although it is commonly called *blue vitriol.* The name vitriol has its origin in the experiments that consisted of heating ferrous sulphate and absorbing the evolved gas in water. The acid thus obtained was called *oil of vitriol* :

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

$$SO_3 + H_2O + H_2SO_4$$

Sulphate anion can give rise to two kinds of double sulphates :

1. *Alums* : These are double sulphates of monovalent and trivalent cations crystallising with twelve molecules of water. The general formula is $M^IM^{III}(SO_4)_2.12H_2O$. The monovalent cation may be one of Na, K, Rb, Cs, NH_4 while the trivalent cation may be one of Fe, Al, Cr, Mn, Co, Rh, etc. Size of the ions plays an important role. It may be noted that monovalent lithium does not form an alum.

2. *Schonites* : These are the double sulphates of monovalent cation and bivalent cation crystallising with six molecules of water. The general formula is $M^I_2M^{II}(SO_4)_2.6H_2O$. Commonly the monovalent cations are ammonium, sodium and potassium while the bivalent cations are iron, nickel, cobalt etc. Mohr's salt is $(NH_4)_2Fe(SO_4)_2.6H_2O$ and hence belong to the family of schonites.

Sulphuric acid is a fine dehydrating agent. It is used for this purpose in the laboratory. Elements which are above hydrogen in the electrochemical series react with the acid to liberate hydrogen. Those elements below hydrogen react at higher temperature to liberate SO_2 and form the corresponding sulphate :

$$2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + SO_2 + 2H_2O$$

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

Carbon and sulphur are oxidised to the respective oxides by hot H_2SO_4 :

$$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$$

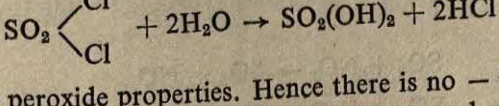
$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

Cellulose present in paper, cotton, wood, etc. are charred on heating with concentrated H_2SO_4 :

$$C_{12}H_{22}O_{11} + 11H_2SO_4 \rightarrow 12C + 11H_2SO_4.H_2O$$

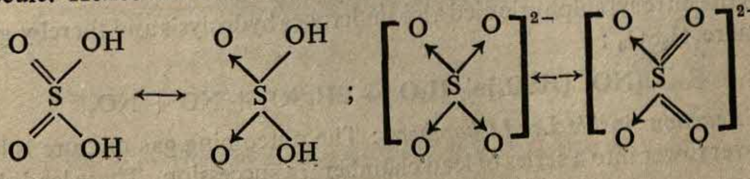
The sulphate salts of the alkaline earths, particularly that of barium, are insoluble in water. Based on this property barium is quantitatively estimated as $BaSO_4$.

Structure : Since the acid gives both acid salts and normal salts it follows that there are two replaceable – OH groups in the acid. This receives support from the fact that hydrolysis of sulphuryl chloride produces this acid :



$$SO_2\begin{cases}Cl\\Cl\end{cases} + 2H_2O \rightarrow SO_2(OH)_2 + 2HCl$$

The acid has no peroxide properties. Hence there is no – O – O – linkage in the molecule. Hence the following resonating structures have been



Excess SO_3 may be dissolved in concentrated H_2SO_4. The resulting acid is known as *fuming sulphuric acid* or *oleum*.

Uses : This acid indeed has too many applications. It is used in the manufacture of fertilisers (eg, superphosphate of lime, ammonium sulphate). It is also profusely used in the syntheses of esters, ethers, sulphate salts and other acids. Fuming sulphuric acid is used in introducing sulphonic acid group ($-SO_3H$) in organic compounds.

Industrial Preparation : There are two methods available for the manufacture of this acid : (*a*) lead chamber process and (*b*) contact process. In both these methods SO_2 is the starting material which is made to get oxidised to SO_3. The sulphur trioxide is then made to react with water to give the acid :

$$2SO_2 + O_2 \rightarrow 2SO_3 \quad ; \quad SO_3 + H_2O \rightarrow H_2SO_4$$

Of the two methods the contact process is the more practised one. A short description of both the methods is given hereafter.

Lead Chamber Process : This is the older method and is used to a limited extent today. Fig. 20. 5 gives the flowsheet diagram of the manufacturing process. The different steps involved are described briefly.

1. *Preparation of* SO_2 : Sulphur or iron pyrites is burnt in air :

$$S + O_2 \rightarrow SO_2 \quad ; \quad 4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

The SO_2 so produced contains good amount of oxygen and nitrogen.

2. *Preparation of* NO_2 : Sodium nitrate and concentrated H_2SO_4 are strongly heated whereby $NaHSO_4$ and HNO_3 are produced initially. The HNO_3 then breaks down into NO_2, O_2 and H_2O. Little SO_2 is also produced.

3. *Dust Removal* : The gases obtained in the above two steps are contaminated with undesirable dust. These gases are led into a dust collector. The dust is allowed to settle down. The issuing gas mixture is more or less free from dust particles.

4. *Reactions inside Glover Tower* : This tower is made of lead plates so that sulphuric acid can do the least damage. This tower is filled with quartz or acid-proof stoneware balls. The dust-free mixture of SO_2, NO_2 and O_2 is introduced through the bottom while 60-65% H_2SO_4 is allowed to flow from the top in the form of a spray. The acid used for spraying the gas mixture comes from the lead chambers which produce the major amount of the sulphuric acid. This acid contains some nitrosyl-sulphuric acid [NO] [HSO_4]. In this tower some SO_2 is changed to H_2SO_4 :

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Some of the nitrosyl sulphuric aicd also undergoes hydrolysis and thereby generates some more H_2SO_4 :

$$2[NO]\ [HSO_4] + H_2O \rightarrow 2H_2SO_4 + NO + NO_2$$

5. *Reaction inside Lead Chambers* : The outcoming gas mixture is led from the Glover tower into a series of lead chambers in succession. These lead chambers

are usually water cooled vertical towers about 40 feet in height and about 20 feet in diameter. In order to minimise corrosion by the acid these chambers are made of lead. Water is sprayed here from the top of the towers while the reactant gases are pushed through the sides. Most of the SO_2 undergoes oxidation to the trioxide which then reacts with water to give H_2SO_4 :

$$SO_2 + NO_2 \rightarrow SO_3 + NO \quad ; \quad SO_3 + H_2O \rightarrow H_2SO_4$$

The air present in the mixture helps to bring about oxidation of the NO to NO_2 which in turn oxidises more of the SO_2 to SO_3 :

$$2NO + O_2 \rightarrow 2NO_2 \quad ; \quad SO_2 + NO_2 \rightarrow SO_3 + NO$$

If there is any deficiency of water in the lead chambers nitrosylsulphuric acid, $[NO][HSO_4]$, often crystallises. These colourless crystals are also often called *chamber crystals.*

6. *Reactions inside Gay-Lussac Tower* : The issuing gases from the lead chambers are introduced through the bottom side of the Gay-Lussac tower while about 75% H_2SO_4 is allowed to flow as spray from the top of the tower. This

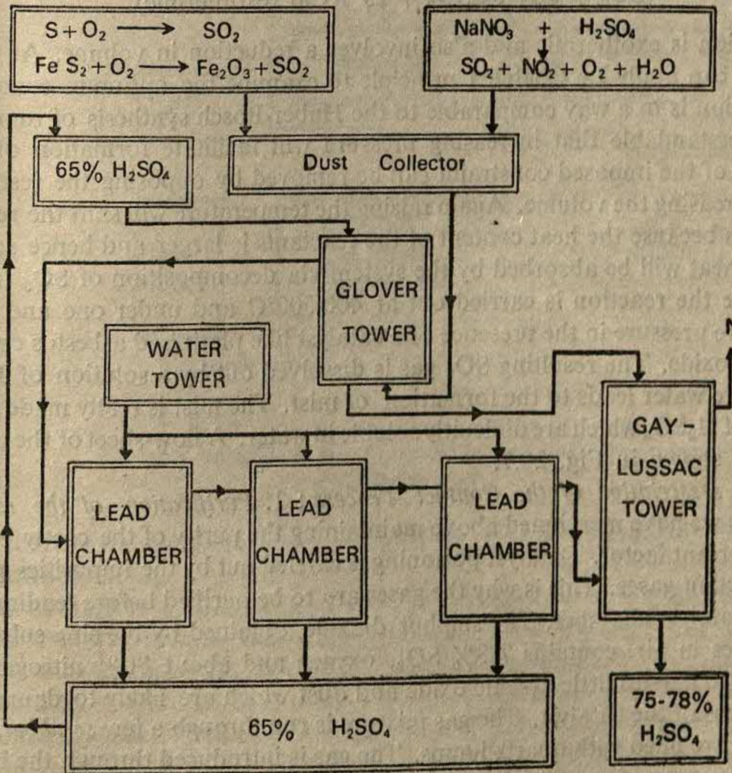


Fig. 20.6. Flow sheet diagram of lead chamber process of manufacture of sulphuric acid

tower is also made of lead and is filled with lumps of quartz. The gases coming out of the lead chambers are mainly NO and N_2. The nitric oxide is absorbed by the 75% H_2SO_4 to produce [NO] [HSO_4]. This nitrosylsulphuric acid alongwith the sulphuric acid is pumped back to the top of the Glover tower. Several operations give 75-78% H_2SO_4 through the bottom of the Gay-Lussac tower. The only gas that issues from the Gay-Lussac tower is nitrogen.

Now we may take a look at the ultimate happenings in the chamber process. We started with a mixture of SO_2, NO_2, O_2 and N_2. After a series of operations in the Glover tower, lead chambers and Gay-Lussac towers we are left with nitrogen. Thus the oxides of nitrogen are the real carriers of oxygen to the SO_2 and hence these oxides may be viewed as the effective agents in the conversion of SO_2 to SO_3.

Contact Process : We have just seen that in the lead chamber process oxides of nitrogen are the real agents which initiate the conversion of SO_2 to SO_3 in the presence of air. In the modern and much used contact process the catalyst used is either platinised asbestos or vanadium pentoxide. One major problem in this process is maintaining the purity of the catalyst. The reaction involved is :

$$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3 + 23 \text{ KCal (exothermic)}$$

The reaction is exothermic and also involves a reduction in volume. At equilibrium we can apply Le Chatelier principle to examine the optimum conditions. This reaction is in a way comparable to the Haber-Bosch synthesis of ammonia. It is understandable that increasing pressure will facilitate formation of SO_3. The effect of the imposed constraint can be removed by opposing the restriction i.e. by decreasing the volume. Again raising the temperature will shift the reaction backwards because the heat content of the reactants is larger and hence some of the extra heat will be absorbed by the system via decomposition of SO_3 to SO_2. In practice the reaction is carried out at 400-500°C and under one and a half atmosphere pressure in the presence of a catalyst like platinised asbestos or vanadium pentoxide. The resulting SO_3 gas is dissolved out by a solution of H_2SO_4. Use of pure water leads to the formation of mist. The mist is really made of fine particles of H_2SO_4 which are difficultly soluble in water. A flow-sheet of the contact process is shown in Fig. 20.7.

Brief Description of the Contact Process : 1. *Purification of the reactant gases* : As we have mentioned above maintaining the purity of the costly catalyst is an important factor. Catalyst poisoning is carried out by the impurities present in the reactant gases. This is why the gases are to be purified before leading them into the catalyst chamber. The sulphur dioxide, obtained by burning sulphur or iron pyrites in air, contains 7-8% SO_2, oxygen and about 80% nitrogen. The mixture also carries little arsenic oxide and dust which are likely to damage the effectiveness of the catalyst. The gas mixture is run through a few *scrubbers*. The scrubbers are filled with quartz lumps. The gas is introduced through the bottom while a fine spray of water is allowed to flow from the top. The gas is then washed with a very dilute solution of NaOH. These manipulations get rid of dust as well as the arsenic oxide. The gas so purified cannot poison the catalyst any more.

2. *Conversion of SO_2 to SO_3* : The purified gas mixture is next led into heat exchangers where the gas is heated upto about 400°C. Thereafter the mixture is forced into the catalyst chambers which contain either platinised asbestos (or sometimes anhydrous magnesium sulphate coated with finely divided platinum) or vanadium pentoxide. The gas is made to react under one and a half atmosphere pressure and a temperature of 400-500°C.

$$2SO_2 + O_2 \xrightarrow[1\frac{1}{2}\text{atm/pt/}V_2O_5]{400\text{-}500°C} 2SO_3$$

The catalyst chambers consist of several tubes packed with the powdered catalyst. The pure gas mixture consisting of SO_2, O_2 and N_2 pass through these catalyst-packed tubes in succession. The out-coming gas contains mostly SO_3 and N_2 alongwith little O_2.

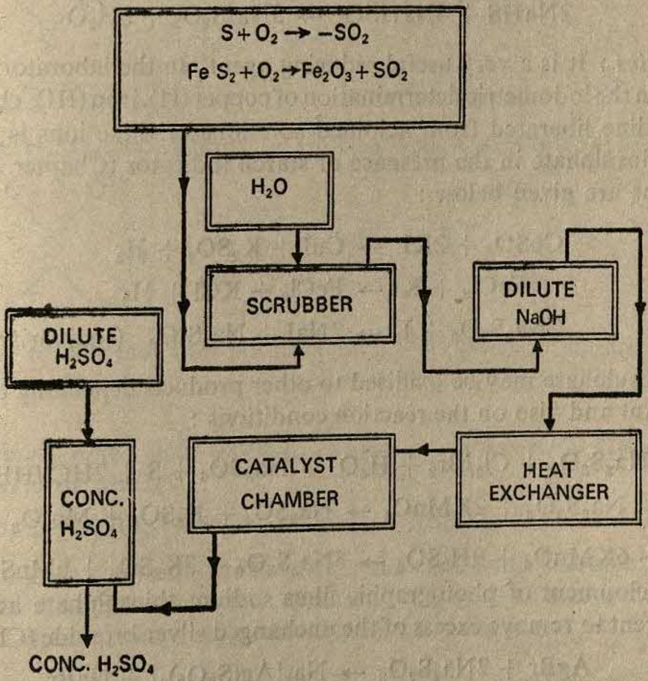


Fig. 20.7. Flow sheet diagram of contact process of manufacture of sulphuric acid

3. *Conversion of SO_3 to H_2SO_4* : The issuing gas is then led into towers, packed with quartz balls, through the bottom. From the top of the towers flows down a fine stream of dilute sulphuric acid. Sometimes even 98% H_2SO_4 is used to absorb the sulphur trioxide to get *fuming sulphuric acid* or *oleum*. Oleum may be chemically formulated as pyrosulphuric acid $H_2S_2O_7$. The oleum may be carefully diluted with water to get sulphuric acid of any desired concentration :

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7 \ ; \ H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

20.10.5. Thiosulphuric Acid : This acid is unstable but many of its salts are too well known. Some of these salts, particularly sodium thiosulphate is of enormous value as a reagent in the laboratory and as a developer in photography. Sodium thiosulphate can be prepared by the following methods :

1. Sodium thiosulphate is formed on boiling a solution of sodium sulphite with powdered sulphur. The compound crystallises with five molecules of water :

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3\ (+\ 5H_2O) \rightarrow Na_2S_2O_3.5H_2O$$

2. Sodium thiosulphate is obtained also via reaction of sodium bisulphite and sodium hydrosulphide :

$$2NaHS + 4NaHSO_3 \rightarrow 3Na_2S_2O_3 + 3H_2O$$

Properties : It is a very useful reducing agent. In the laboratory it is extensively used in the iodometric determination of copper (II), iron (III), chromium (VI) etc. The iodine liberated from acidified solutions of these ions is titrated with standard thiosulphate in the presence of starch indicator (Chapter 29). Some of the reactions are given below :

$$CuSO_4 + 2KI \rightarrow CuI + K_2SO_4 + \frac{1}{2}I_2$$

$$FeCl_3 + KI \rightarrow FeCl_2 + KCl + \frac{1}{2}I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6 \quad \text{(sodium tetrathionate)}$$

Sodium thiosulphate may be oxidised to other products depending on the power of the oxidant and also on the reaction conditions :

$$Na_2S_2O_3 + Cl_2/Br_2 + H_2O \rightarrow Na_2SO_4 + S + 2HCl/HBr$$

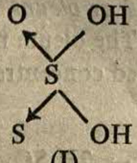
$$Na_2S_2O_3 + 2KMnO_4 \rightarrow Na_2SO_4 + K_2SO_4 + Mn_2O_3$$

$$5Na_2S_2O_3 + 6KMnO_4 + 9H_2SO_4 \rightarrow 5Na_2S_2O_6 + 3K_2SO_4 + 6MnSO_4 + 9H_2O$$

During development of photographic films sodium thiosulphate acts as a complexing reagent to remove excess of the unchanged silver bromide (Chapter 24) :

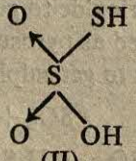
$$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

Structure : There is a connection between the structures of sodium sulphate and sodium thiosulphate. Addition of one oxygen to Na_2SO_3 leads to Na_2SO_4 while addition of one sulphur gives $Na_2S_2O_3$. Thus we observe that the thiosulphate ion is obtained by the substitution of one of the four oxygen atoms of the tetrahedral sulphate ion by a sulphur atom. Since thiosulphate is a binegative ion the acid must have two replacable hydrogens i.e. the acid must have either (*a*) two –OH groups or (*b*) one –OH and one –SH group.



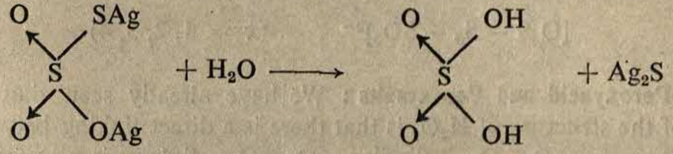
(I)

or

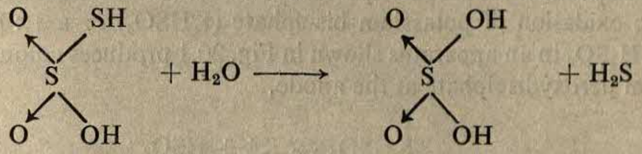


(II)

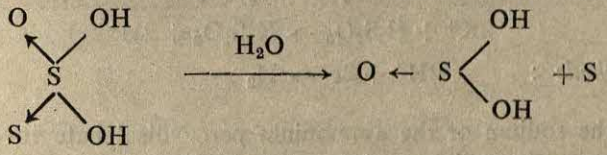
Sodium thiosulphate reacts with silver nitrate to give silver thiosulphate which undergoes hydrolysis to precipitate Ag_2S :



Although this hydrolysis supports the – HS containing structure (II) but this strucutre also demands formation of H_2S and H_2SO_4 on acidification of $Na_2S_2O_3$.



In fact we get H_2SO_3 and sulphur – which supports structure (I) :



Thus we have to conclude that both the structures (I) and (II) are possible for thiosulphuric acid.

20.10.6 Dithionic Acid : This oxyacid, $H_2S_2O_6$, is obtained by the oxidation of sulphurous acid by MnO_2 :

$$MnO_2 + 2H_2SO_3 + 4HCl \rightarrow MnCl_2 + H_2S_2O_6 + 2HCl + 2H_2O$$

On neutralising the solution with baryta the barium salt of dithionic acid BaS_2O_6. is obtained in the crystalline form. Both the sulphurs are tetrahedral and there is a sulphur-sulphur bond : $O_3S - SO_3$ in the dithionate ion.

20.10.7. Polythionic Acids : These have the general formula $H_2S_nO_6$ (n = 3, 4, 5, 6). Most of these acids are unstable. On saturating a cold aqueous solution of SO_2 with H_2S many complex reactions take place. The solution thus obtained is known as *Wackenroder's solution*. This solution contains mostly pentathionic acid and tetrathionic acid :

$$H_2S + 2SO_2 \rightarrow 3SO + H_2O \;;\; 5SO + H_2O \rightarrow H_2S_5O_6$$

However for the purpose of syntheses of particular polythionate salt special methods are nowadays applied :

Trithionate : $2Na_2S_2O_3 + 4H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4H_2O$

Tetrathionate : $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

Pentathionate : $5Na_2S_2O_3 + 6HCl \xrightarrow[-10°C]{As^{3+}} 2Na_2S_5O_6 + 6NaCl + 3H_2O$

The structures of these polythionates have been found to be the following as deduced from X-ray crystallographic methods :

$$[O_3S - S_x - SO_3]^{2-} \qquad (x = 1, 2, 3, 4)$$

20.10.8. Peroxyacid and Peroxysalts : We have already seen that the special feature of the structure of H_2O_2 is that there is a direct linking between the two oxygen atoms : $-O-O-$. Similar $-O-O-$ linkage is also found in some oxyacids and their salts. Such compounds are known as peroxyacids and peroxysalts. Most important of these compounds are found in the sulphur oxyacids.

Anodic oxidation of potassium bisulphate ($KHSO_4$) or a 1 : 1 mixture of K_2SO_4 and H_2SO_4 in an apparatus shown in Fig. 20.1 produces colourless crystals of potassium peroxydisulphate at the anode.

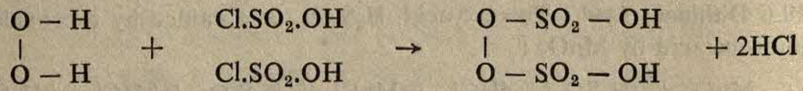
$$KHSO_4 \rightarrow K^+ + HSO_4^-$$

at the anode : $$2HSO_4^- \rightarrow H_2S_2O_8 + 2e$$

$$2K^+ + H_2S_2O_8 \rightarrow K_2S_2O_8 + 2H^+$$

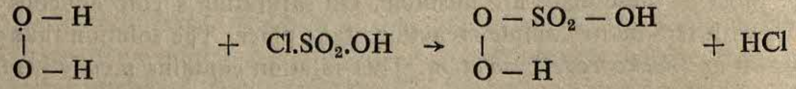
at the cathode : $$2H^+ + 2e \rightarrow H_2$$

Syntheses of the sodium or the ammonium peroxydisulphate involves similar anodic oxidation of the sodium or the ammonium bisulphates. Anodic oxidation of H_2SO_4(50%) gives a solution of peroxydisulphuric acid $H_2S_2O_8$. This acid can also be prepared by the reaction of H_2O_2 and chlorosulphonic acid HSO_3Cl :



$$\begin{array}{l} O-H \\ | \\ O-H \end{array} + \begin{array}{l} Cl.SO_2.OH \\ \\ Cl.SO_2.OH \end{array} \rightarrow \begin{array}{l} O-SO_2-OH \\ | \\ O-SO_2-OH \end{array} + 2HCl$$

On distilling the above mixture under very low pressure crystals of $H_2S_2O_8$ (M.P. 65°C) are obtained. This acid is known as Marshall's acid. Hydrolysis of this peroxyacid gives a second acid, namely peroxymonosulphuric acid H_2SO_5 : $H_2S_2O_8 + H_2O \rightarrow H_2SO_4 + H_2SO_5$. Peroxymonosulphuric acid may be obtained by the following reaction :



$$\begin{array}{l} O-H \\ | \\ O-H \end{array} + Cl.SO_2.OH \rightarrow \begin{array}{l} O-SO_2-OH \\ | \\ O-H \end{array} + HCl$$

Peroxymonosulphuric acid is known as Caro's acid and has a melting point 45°C.

Peroxysulphates are among the most used reagents in a chemical laboratory. They are very good oxidants. The reduction potential of $S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$ is $+2.01$ volts. This high positive potential speaks of its strong oxidising power. The ion can readily oxidise ferrous to ferric, manganese (II) to permanganate (via Ag^+) iodide to iodine etc. During the syntheses of complexes of metal ions in their higher oxidation states sodium or potassium peroxydisulphate is the most preferred oxidant. These salts have been used in the oxidation of silver (I) to silver (II), manganese (II) to manganese (IV), nickel (II) to nickel (III/IV), copper (II) to copper (III) etc. Some of the common oxidising reactions are given below :

$$2FeSO_4 + K_2S_2O_8 \rightarrow Fe_2(SO_4)_3 + K_2SO_4$$

$$2MnSO_4 + 5K_2S_2O_8 + 8H_2O \rightarrow 2KMnO_4 + 4K_2SO_4 + 8H_2SO_4$$

$$2KI + K_2S_2O_8 \rightarrow I_2 + 2K_2SO_4$$

$$K_2S_2O_8 + 2AgNO_3 + 2H_2O \rightarrow 2AgO + 2KHSO_4 + 2HNO_3$$

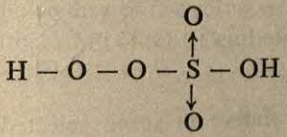
Peroxy compounds decolourise the violet colour due to permanganate in acid medium. In presence of acids the peroxy compounds produce H_2O_2 which reduces permanganate to manganese (II) :

$$K_2S_2O_8 + H_2SO_4 \rightarrow H_2S_2O_8 + K_2SO_4$$

$$H_2S_2O_8 + 2H_2O \rightarrow H_2O_2 + 2H_2SO_4$$

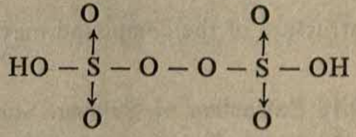
$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$$

Structure : Permonosulphuric acid and peroxydisulphuric acids may be represented by the following structures :



$$H - O - O - \overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}} - OH$$

(H_2SO_5)



$$HO - \overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}} - O - O - \overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}} - OH$$

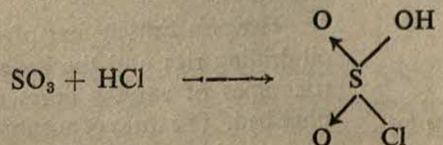
($H_2S_2O_8$)

Distincition between a peroxy salt and a per salt : The qualifying term *peroxy* conveys the idea that the compound concerned contains the peroxy (— O — O —) linkage. Thus H_2O_2 and $K_2S_2O_8$ are true peroxy compounds. The term *per*, on the other hand, means something higher. Thus $KMnO_4$ is called permanganate to indicate that it is something higher than manganate i.e. manganese has a valence + 7 in $KMnO_4$ while in manganate manganese has a valence + 6. It is often loosely said that $K_2S_2O_8$ is persulphate but this naming does not surely convey the meaning that we have a genuine peroxy (— O — O —) linkage in the compound.

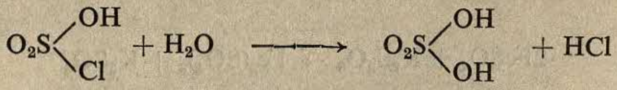
20.10.9. OXYHALIDES OF SULPHUR

We discuss below three important oxyhalides, namely chlorosulphonic acid, sulphuryl (sulphonyl) chloride and thionyl (sulphinyl) chloride.

Chlorosulphonic Acid : This acid, HSO_3Cl may be viewed to be formed by the substitution of one OH groups of H_2SO_4 by a —Cl group. This is prepared by passing dry HCl gas through fuming sulphuric acid ($H_2SO_4 + SO_3$)



It undergoes vigorous hydrolysis :



$$O_2S\begin{matrix} \diagup OH \\ \diagdown Cl \end{matrix} + H_2O \longrightarrow O_2S\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} + HCl$$

This acid finds use in organic synthetic work for introducing $-SO_3H$ group :

$$C_6H_6 + O_2S(OH)Cl \rightarrow C_6H_5 - SO_3H + HCl$$

Sulphuryl (*sulphonyl*) *Chloride* : This acid, SO_2Cl_2, may be viewed to be formed by the substitution of the two $-$ OH groups of H_2SO_4 by two $-$ Cl groups. The compound is formed by interacting SO_2 and Cl_2 in the presence of catalysts like camphor, charcoal and acetic anhydride. This may also be obtained by boiling chlorosulphonic acid in the presence of mercury sulphate :

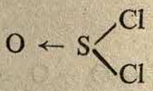
$$SO_2 + Cl_2 \rightarrow SO_2Cl_2 \quad ; \quad 2HSO_3Cl \rightarrow SO_2Cl_2 + H_2SO_4$$

The compound is obtained pure by fractional distillation (B.P. of SO_2Cl_2, 69°C).

Thionyl (*sulphinyl*) *Chloride* : This compound, $SOCl_2$, is obtained by the reaction of SO_3 and PCl_5 followed by fractional distillation (B.P. $SOCl_2$, 87°C ; $POCl_3$, 107°C) :

$$SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3$$

The structure of the compound may be represented as :



$$O \leftarrow S\begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$$

20.10.10 Extraction of Sulphur. Sulphur occurs native in some selected places over the world. Notable among these countries are Japan, Italy and the United States. Most of the world's sulphur comes from Texas and Louisiana states of U.S.A. Sulphur also occurs in the combined state in important ores like galena (PbS), iron pyrites (FeS_2), cinnabar (HgS), gypsum ($CaSO_4.2H_2O$) etc.

1. *Herman Frasch Process of extracting Sulphur* : The huge deposit of native sulphur in the U.S.A. is about 400 feet below the surface of the earth. Above the bed of this sulphur there are layers of clay, limestone and sand. The enormous problem of bringing the sulphur from so much below the surface level was solved by the American scientist and engineer Herman Frasch.

The sulphur deposit in Texas and Louisians is at least 70% sulphur with very little impurities.

Herman Frasch first of all dug well with oil-drilling rigs and the lowered three concentric pipes of varying bores right into the sulphur bed. The three concentric pipes were encased into a big iron pipe. Through the outermost

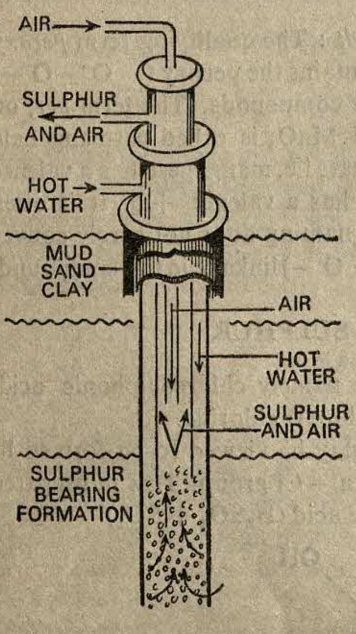


Fig. 20.8. Frasch process for extracting sulphur

pipe of about six inch diameter superheated steam (170-180°C) under a pressure of 140 pounds per square inch was forced onto the sulphur bed. This caused the sulphur to melt. Through the innermost tube of about one-inch bore compressed air was forced onto the sulphur bed. As a result of these two simultaneous operations molten sulphur was brought to the surface in the form of foam through the middle pipe of about three-inch bore. This sulphur was collected in large wooden buckets. Such a sulphur well provides about 500 tons of nearly 100% pure sulphur per day. The process is also relatively cheap.

Today the United States is the largest producer and also the largest exporter of this important raw material. Credit for this spectacular achievement, however, goes to Herman Frasch who carried our civilisation a step forward.

2. *Extraction of Sulphur from some Compounds* : Most of the metal sulphides on burning in air produces sulphur dioxide. The SO_2 gas is washed with sodium sulphite solution when sodium bisulphite is produced :

$$Na_2SO_3 + SO_2 + H_2O \rightleftharpoons 2NaHSO_3$$

Some $AlCl_3$ is kept dissolved in the sodium sulphite solution. On heating the sodium bisulphite solution the reaction runs backwards and pure SO_2 is given off. The acidity of the solution developed due to hydrolysis of $AlCl_3$ also helps in the liberation of the SO_2 gas. The pure SO_2 gas is then reacted with white-hot (1000°C) coke to force reduction :

$$SO_2 + C \rightarrow CO_2 + S$$

On cooling sulphur vapour condenses to the solid state.

Properties : It is one of the most important non-metals. It gives rise to a number of allotropic forms. On burning in air we get SO_2. On heating elementary sulphur reacts with many metals and non-metals to produce important sulphides :

$$Fe + S \rightarrow FeS \quad ; \quad 2Na + S \rightarrow Na_2S$$
$$2S + Cl_2 \rightarrow S_2Cl_2 \quad ; \quad C + 2S \rightarrow CS_2$$

Sulphur gets oxidised to H_2SO_4 on treating with HNO_3 :

$$S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

Powdered sulphur reacts with ammoniacal solution of H_2S to give yellow polysulphides :

$$(NH_4)_2S + S_{x-1} \rightarrow (NH_4)_2S_x$$

Uses : Its major use is in the manufacture of H_2SO_4. It is also used in the manufacture of important compounds like sulphur bearing organic dyes, sodium thiosulphate, in explosives and in insecticides.

EXERCISES

1. Give an account of the allotropic modifications of oxygen and sulphur.
2. Present a comparative study of the chemistry of oxygen and sulphur.
3. Oxygen is bivalent in all its compounds while sulphur exhibits more than one valence. How do you explain this difference?

4. What are peroxides and peroxysalts? Is there any fundamental difference between peroxysalts and permanganate and perchlorate?

5. Describe the synthesis of potassium peroxydisulphate. How would you get Marshall's acid, Caro's acid and hydrogen peroxide from the above salt?

6. Give an account of the synthesis, properties and structure of ozone.

7. What is sulphuretted hydrogen? How does it influence the qualitative scheme of analysis of metal ions?

8. Write short accounts of the following :
(*a*) alums (*b*) schonites (*c*) vitriols (*d*) electronic structure of SO_2, SO_3, $SOCl_2$, SO_2Cl_2

9, Describe the synthesis, properties, uses and structure of sodium thiosulphate.

10. What experiments would allow us to distinguish between ozone and hydrogen peroxide?

11. Give two examples in each case to show that SO_2 and H_2O_2 can act both as an oxidising agent and a reducing agent.

12. Complete the following reactions :

(*a*) $Na_2S_2O_3 + Cl_2 + H_2O \rightarrow$
(*b*) $KMnO_4 + H_2O_2 + H_2SO_4 \rightarrow$
(*c*) $FeSO_4 + K_2S_2O_8 \rightarrow$
(*d*) $Na_2S_2O_3 + I_2 \rightarrow$
(*e*) $KMnO_4 + H_2O_2 + H_2SO_4 \rightarrow$
(*f*) $KMnO_4 + SO_2 + H_2O \rightarrow$
(*g*) $K_2Cr_2O_7 + H_2SO_4 + SO_2 \rightarrow$
(*h*) $Ag + H_2SO_4 \rightarrow$

13. Describe the contact process of manufacture of H_2SO_4.

CHAPTER 21

GROUP VIIB. THE HALOGENS

21.1. INTRODUCTION

The elements fluorine, chlorine, bromine, iodine and finally astatine are members of this group. The Greek term *hals* means sea salts. During the seventeenth and the eighteenth centuries chemists were successful in extracting the elements chlorine, bromine and iodine from sea salts and sea weeds. Hence these elements have been given the family name *halogens.* Much later Moissan was able to isolate fluorine via electrolysis of fused fluorides. We shall confine our discussion of this group to the first four members. The halogens form one of the most coherent groups in the entire periodic table.

21.2. A COMPARATIVE STUDY OF THE HALOGENS

Physical Properties : 1. The electron distribution of the outermost subshells of the elements of this group is s^2p^5. The members closest to the halogens on to the right of the table are the noble gases neon, krypton, argon, and xenon with a filled subshell electronic configuration s^2p^6. Thus the halogens are just one electron short of the next noble gas (Table 21.1).

Table 21.1. A Comparative Study of the Properties of the Halogens

Element	Atomic Number	Electron Distribution	Ionisation Potential (*ev*)	Atomic Radius (A)	Electro-negativity	Electron Affinity (*ev*)
F	9	$[He]2s^22p^5$	17.42 34.98 62.65 87.14	0.64	4.0	3.62
Cl	17	$[Ne]3s^23p^5$	13.01 23.80 39.90 53.50 67.80	0.99	3.0	3.79
Br	35	$[Ar]3d^{10}4s^2 4p^5$	11.84 21.60 35.90 47.30 59.70	1.14	2.8	3.56
I	53	$[Kr]4d^{10}5s^2 5p^5$	10.45 19.09	1.33	2.5	3.28

2. In view of their proximity to the noble gases it is only expected that their electron affinity and electronegativity will be very high. In fact these are the elements which have the highest electron affinity and electronegativity in their respective period.

3. Because of their high electron affinity it follows that their ionisation potentials will also be quite high i.e. these elements will be reluctant to part with their electron. Hence rarely do we find them in the cationic form. However we know that in a given group of the periodic table basic properties increase with increasing atomic number. Because of this we do find some slight cationic properties in the element iodine.

4. Since these elements are just short of one electron they are usually monovalent. This valence they can exhibit by way of forming mononegative anion or by forming a shared pair covalent bond. Examples of these two classes are NaCl and CCl_4.

5. As expected with increase in atomic number their atomic radii also increase.

Chemical Properties : 1. All the halogens react with hydrogen to form covalent volatile hydrides HX (X = F, Cl, Br and I). The vigorousness of the reaction, however, falls off with increase in the atomic number from fluorine to iodine. HF and HCl are stable to H_2SO_4 but HBr and HI are oxidised by hot concentrated H_2SO_4 to the respective halogens.

2. The halogens react with the most basic elements of the table, namely the alkalies, to form pure ionic halides of the type NaCl etc. These halides have very high melting and boiling points. In the fused state they conduct electricity.

3. Of all the halogens fluorine is the most electronegative. As a consequence hydrogen bonding in HF is the strongest and thus we get an associated liquid. The strength of hydrogen bonding decreases as we move from fluorine to iodine.

4. The halogens form a whole series of complicated oxyacids. In these oxyacids their oxidation number varies, usually in the range $+1$ to $+7$. For a given halogen the acid character of the oxyacid increases with increasing oxidation number of the halogen. On the other hand with the same oxidation number the acid character of the oxyacids falls from chlorine to iodine. No oxyacid of fluorine is known.

21.3. COMPOUNDS OF FLUORINE

21.3.1. Hydrofluoric Acid : This hydride of fluorine, HF, is prepared by the reaction of concentrated H_2SO_4 with fluorspar (CaF_2). The reaction is carried out in a lead retort and the liberated HF is dissolved in water taken in a lead vessel.

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

This acid is a weak one. Because of considerable difference in electronegativities of the two elements there is a strong hydrogen bonding which leads to association. Anhydrous HF is thus a liquid although anhydrous HCl is a gas. HF reacts with silica to produce first SiF_4 and then hydrofluosilicic acid H_2SiF_6 :

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \quad ; \quad SiF_4 + 2HF \rightarrow H_2SiF_6$$

All glass vessels contain silica which is attacked by HF. Hence the solution of the acid is stored in polythene bottles. However the property of attacking glass is made use of in etching glass equipments. In practice glass equipments meant for quantitative measurments are first covered by wax and then marks are made with a sharp marking device. The equipments are then treated with HF acid, which etches galss at the marked points.

Qualitative detections of silicate and fluoride are made by similar techniques. For detection of a fluoride the sample is taken in a dry glass tube and treated with concentrated H_2SO_4. On warming the liberated HF attacks the silica of the glass tube and produces SiF_4. If a drop of water taken in a platinum loop is held over the issuing gas it turns turbid due to the formation of orthosilicic acid :

$$3SiF_4 + 4H_2O \rightarrow H_4SiO_4 + 2H_2SiF_6$$

For the detection of silicate we cannot obviously operate in a glass test tube. The silicate material is taken in a lead crucible provided with a lead cover with a small hole. The silicate is now mixed with CaF_2 and concentrated H_2SO_4 and the crucible heated on an asbestos board. A drop of water in a platinum wireloop is held over the hole on the lid. If a silicate is present the water drop will turn turbid due to the formation of orthos licic acid.

HF reacts readily with BF_3 to form fluoboric acid HBF_4.

21.3.2. Oxides of Fluorine : There are two oxides of fluorine : F_2O and F_2O_2. The second oxide is much too unstable. We describe the first here. The monoxide, F_2O, is formed by bubbling fluorine through a 2% aqueous solution of NaOH. F_2O gas is obtained in about 70% yield :

$$2F_2 + 2NaOH \rightarrow 2NaF + F_2O + H_2O$$

It is interesting to note that a similar reaction between chlorine and dilute alkali gives NaOCl and NaCl.F_2O reacts with KOH to evolve O_2 :

$$F_2O + 2KOH \rightarrow 2KF + O_2 + H_2O$$

The boiling point of F_2O is – 145°C.

21.4. PREPARATION OF FLUORINE

Because of the extreme reactivity of elementary fluorine it proved immensely difficult to get it in elementary form. In nature it always occurs in combination with other elements eg. fluorspar (CaF_2), cryolite (Na_3AlF_6) etc. Let us consider the following reduction potentials :

$$F_2 + 2e \rightleftharpoons 2F^- \quad ; \quad E^\circ = +2.65 \text{ volts}$$

$$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O \quad ; \quad E^\circ = +1.23 \text{ volts}$$

An inspection of the values immediately tells us that it is far easier to get the evolution of oxygen at the anode than of fluorine. It means that it is never possible to get fluorine by electrolysis of aqueous solution of a fluoride. This is also true of liberation of hydrogen at the cathode in preference to the alkali metals :

$$2H^+(10^{-7}M) + 2e \rightleftharpoons H_2 \quad ; \quad E^\circ = -0.42 \text{ volts}$$
$$Na^+ + e \rightleftharpoons Na \quad ; \quad E^\circ = -2.71 \text{ volts}$$

Thus we see that if we have to get fluorine via electrolysis we must use some anhydrous and fused fluoride as the electrolyte. Then the next problem is to find the right kind of material to be used in the construction of the electrolytic cell. It should be appreciated that fluorine is one of the most active corrosive elements and would attack most materials used in the making of the cell. Moissan used the costly alloy made of platinum and iridium. Nowadays the electrolysis is carried out in a V-shaped cell made of heavy copper. The electrolytic cell is commonly of 2 inch diameter. The two sides of the cell are provided with two exits for the gases liberated at the two electrodes. Graphite electrodes of about 300 mm in length and 5 mm in diameter are introduced into the two sides of the cell and are kept fixed with cement. The entire cell is covered with asbestos. The anode side tube is connected with two copper U-tubes packed with NaF to arrest any HF.

KHF_2 is fused and is used as the electrolyte. A current of strength of 5 — 10 amperes and 12 — 18 volts is applied. Hydrogen is liberated at the cathode and fluorine at the anode. The fluorine is allowed to flow through two U-tubes to arrest any HF : $NaF + HF \rightarrow NaHF_2$.

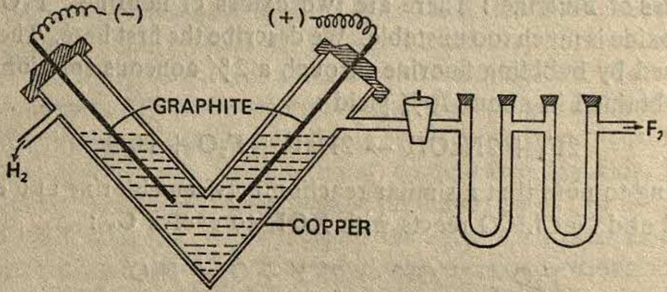


Fig. 21.1. Electrolysis of fused KHF_2

$$KHF_2 \rightleftharpoons KF + HF \rightleftharpoons K^+ + H^+ + 2F^-$$

at the cathode : $2H^+ + 2e \rightarrow H_2$

at the anode : $2F^- \rightarrow F_2 + 2e$

Properties : Of all the elements in the periodic table fluorine is the most electronegative. Thus most of the metal fluorides are ionic in nature. HF is covalent but due to a considerable difference in the electronegativities of the two elements there is strong polarity in the molecule. This leads to association $(HF)_n$. With the exceptions of a few elements like platinum, iridium most others are affected by this gas. It is also not much reactive towards oxygen and nitrogen under ordinary circumstances. Some of the sample reactions are given below :

$$2F_2 + 2H_2O \rightarrow 4HF + O_2$$

$$F_2 + H_2 \rightarrow 2HF$$

$$F_2 + 2HCl \rightarrow 2HF + Cl_2$$

Fluorine forces other elements to exhibit their maximum coordination numbers eg. SF_6, PF_5, $[SF_6]^{2-}$, $[BF_4]^-$, OsF_8 etc. Fluorine also reacts vigorously with many organic compounds :

$$CCl_4 + 2F_2 \rightarrow CF_4 + 2Cl_2$$

Fluorine is decidedly the most oxidising of all the elements in the periodic table.

21.4.1. Special Characteristics of Fluorine : Compared to the other three members of the halogen family fluorine has several specialities. These characteristics originate from its small size, highest electronegativity, high electron affinity and absence of *d*-orbitals.

1. Its electronegativity is the highest (4.0).
2. Because of the very high electronegativity HF is very strongly hydrogen bonded. Its melting and boiling points are thus abnormal.
3. Of the halogens it is the smallest in size and at the same time the most electronegative. These two properties bring out the highest coordination numbers of many other elements : SF_6, OsF_8, $[SiF_6]^{2-}$ etc.
4. Solubilities of many fluorides are unusual compared to those of the other halides. Thus AgCl, AgBr and AgI are insoluble in water but AgF is quite soluble. $CaCl_2$, $CaBr_2$ and CaI_2 are highly soluble but CaF_2 is quite insoluble.
5. The fluorides are likely to be the most ionic in nature. Thus following Fajans' rules chlorides, bromides and iodides of tin (IV) and aluminium (III) are covalent but SnF_4 and AlF_3 are ionic in nature.

21.5. COMPOUNDS OF CHLORINE

21.5.1. Hydrogen Chloride and Hydrochloric Acid : *Industrial Preparation* : In the industrial preparation of salt cake (Na_2SO_4) hydrogen chloride gas is obtained as a by-product. Common salt is taken in big, shallow iron pans and is reacted with concentrated H_2SO_4 at red heat. The reactions are carried out in chambers constructed of fire-proof bricks. These chambers are provided with outlets near the top to serve as exits of HCl gas. The outlets are also made of corrosion resistant materials.

The reaction between NaCl and H_2SO_4 is completed in two chambers. In the first chamber sufficient H_2SO_4 is added to the NaCl so that the normal salt Na_2SO_4 may be produced. But the formation of the normal salt takes place via the acid salt $NaHSO_4$. In the first chamber the temperature is maintained close to 200°C when the acid sulphate i.e. the bisulphate is produced :

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

The evolved HCl gas is led out through the exit at the top. The $NaHSO_4$ and the unreacted NaCl left in the iron pan is then transferred into the second chamber

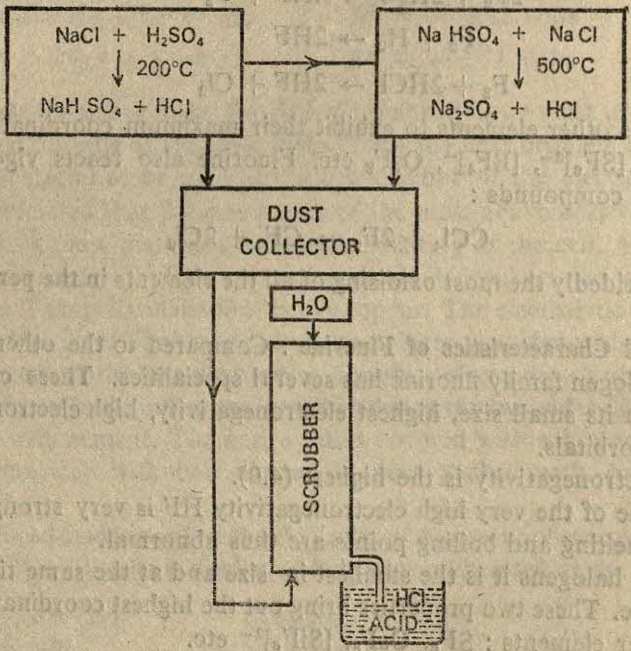


Fig. 21.2. Flowsheet diagram of the manufacture of HCl

where the temperature is around 500°C. Hence the reaction goes to completion :

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$$

The HCl given off here is taken out through the exit of the second chamber. The HCl from the two reaction chambers is led through a dust collectror packed with coke and then forced through the bottom of a scrubber. Here the upward moving HCl gas is sprayed with water from the top. The hydrochloric acid so produced is about 35% by weight i.e. $12N$. The acid is collected through a side tube near the lower portion of the scrubber.

Industrial Preparation from Electrolytic Hydrogen and Chlorine : In some industrial operations eg. in the electrolysis of saturated brine we get hydrogen at the cathode while chlorine is liberated at the anode. These two gases are fired in a silica furnace when HCl gas is formed :

$$H_2 + Cl_2 \rightarrow 2HCl$$

The HCl gas is then treated as described above to give hydrochloric acid.

Laboratory Method of Preparation : Usually HCl gas is obtained in the laboratory by two different methods.

1. *Adaptation of Le Blanc Procedure* : Concentrated H_2SO_4 is allowed to drop over common salt :

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

2. *Reaction between hydrochloric acid and concentrated* H_2SO_4 : Concentrated H_2SO_4 is allowed to drop over concentrated HCl acid. The concentrated sulphuric acid effectively extracts the water from HCl solution:

$$H_3O^+Cl^- + H_2SO_4 \rightarrow \uparrow HCl + H_2SO_4(H_2O)$$

Properties : In the gaseous state it is a covalent compound and is a non-conductor of electricity. But in aqueous solution it exists as hydrochloric acid, $H_3O^+Cl^-$, and then becomes a conductor. The acid readily reacts with those metals placed above hydrogen in the electrochemical series and forms their chloride alongwith evolution of hydrogen :

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$
$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

Hydrochloric acid reacts with those elements placed below hydrogen in the electrochemical series only in the presence of oxygen or some other oxidants :

$$2Cu + 4HCl + O_2 \rightarrow 2CuCl_2 + 2H_2O$$

It does not react with any nonmetal element except fluorine :

$$2HCl + F_2 \rightarrow 2HF + Cl_2$$

It reacts with salts of mild acids to displace the weak anion :

$$FeS + 2HCl \rightarrow H_2S + FeCl_2$$

HCl reacts with strong oxidants and gets oxidised to chlorine :

$$4HCl + MnO_2 \rightarrow MnCl_2 + Cl_2 + 2H_2O$$
$$16HCl + 2KMnO_4 \rightarrow 2MnCl_2 + 2KCl + 5Cl_2 + 8H_2O$$
$$3HCl + HNO_3 \rightarrow 2H_2O + NOCl + Cl_2$$

In aqueous solution it produces precipitates of insoluble chlorides with some metal ions :

$$AgNO_3 + HCl \rightarrow AgCl + HNO_3$$
$$Pb(NO_3)_2 + 2HCl \rightarrow PbCl_2 + 2HNO_3$$

21.5.2. Oxides of Chlorine : Four chlorine oxides are known :

Oxide :	chlorine monoxide	chlorine dioxide	dichlorine hexoxide	dichlorine heptoxide
formula :	Cl_2O	ClO_2	Cl_2O_6	Cl_2O_7
oxidation number	+1	+4	+6	+7

In accordance with general rule the oxidising power and acid character of these oxides should increase with increasing oxidation number.

Chlorine Monoxide : This oxide, Cl_2O, is obtained by passing chlorine gas over freshly precipitated mercuric oxide :

$$2Cl_2 + 2HgO \rightarrow HgO.HgCl_2 + Cl_2O$$

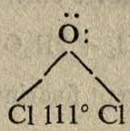
This oxide may be looked upon as the anhydride of hypochlorous acid :

$$Cl_2O + H_2O \rightarrow 2HOCl$$

Chlorine monoxide reacts with alkali solution to give alkali hypochlorites :

$$Cl_2O + 2NaOH \rightarrow 2NaOCl + H_2O$$

The structure of this compound has been evaluated. Oxygen uses roughly sp^3 hybrid orbitals to overlap with the two $3p$ orbitals of the two chlorines with an unpaired electron on each. The two remaining hybrid orbitals of oxygen carry the two lone pairs of electrons.



O – Cl = 1.71A
<Cl – O – Cl = 111°

Chlorine Dioxide : This oxide, ClO_2, may be obtained by two methods :

1. Dry chlorine and silver chlorate ($AgClO_3$) react around 90°C to evolve this oxide of boiling point 11°C. On cooling the dioxide can be recovered pure :

$$2AgClO_3 + Cl_2 \rightarrow 2AgCl + 2ClO_2 + O_2$$

2. Potassium chlorate and oxalic acid react around 60°C to give ClO_2 :

$$2KClO_3 + 2H_2C_2O_4 \rightarrow K_2C_2O_4 + 2H_2O + 2ClO_2 + 2CO_2$$

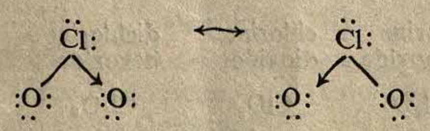
It is a yellow coloured gas. In aqueous solution it gives both chlorous and chloric acid :

$$2ClO_2 + H_2O \rightarrow HClO_2 + HClO_3$$

It liberates iodine from acidified KI :

$$2ClO_2 + 10KI + 8HCl \rightarrow 10KCl + 4H_2O + 5I_2$$

Chlorine dioxide is one of the few odd electron compounds. The O – Cl – O bond angle is 117° indicating that chlorine is using sp^2 hybrid orbitals. The structure may be viewed as the resonance hybrid of the following two forms :



<O – Cl – O = 117°
O – Cl = 1.49A

Dichlorine Hexoxide : This oxide, Cl_2O_6, is formed on mixing ClO_2 and ozone :

$$2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2$$

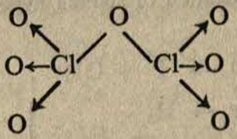
The oxide is a red coloured liquid. Determination of its molecular weight in CCl_4 shows it to have the dimeric formula Cl_2O_6. It reacts with alkalies to produce chlorate and perchlorate :

$$Cl_2O_6 + 2NaOH \rightarrow NaClO_3 + NaClO_4 + H_2O$$

Chlorine Heptoxide : This oxide, Cl_2O_7, is the anhydride of perchloric acid. The oxide can be obtained by dehydrating perchloric acid by P_4O_{10} at − 10°C. It can be distilled pure around 85°C. It reacts with alkalies to give perchlorates :

$$Cl_2O_7 + 2NaOH \rightarrow 2NaClO_4 + H_2O$$

Its possible structure is as shown below :



21.5.3. Oxyacids of Chlorine : There are four well known oxyacids and their salts. These oxyacids are : hypochlorous acid HClO, chlorous acid $HClO_2$, chloric acid $HClO_3$ and perchloric acid $HClO_4$.

oxyacids :	hypochlorous acid	chlorous acid	chloric acid	perchloric acid
formula :	HClO	$HClO_2$	$HClO_3$	$HClO_4$
oxidation number of chlorine :	+ 1	+ 3	+ 5	+ 7

Hypochlorous acid : Chlorine gas is sparingly soluble in water. The solution produces hypochlorous acid :

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

In alkaline solution chlorine dissolves to give alkali hypochlorites :

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$

Sodium hypochlorite is also obtained via electrolysis of brine (saturated 6*M* NaCl solution). A series of graphite rods serve as electrodes. One of the end graphite rods is made the positive pole while the graphite rod at the other end is made the negative terminal. Through the cell flows a stream of saturated brine solution. Each pair of graphite rods perform as a pair of electrodes. As expected we get evolution of hydrogen at each cathode. Since the solution has a high chloride concentration and evolution of chlorine is favoured at graphite we get evolution of chlorine, rather than of oxygen, at the anode. Evolution of hydrogen makes the solution alkaline due to release of OH^- ions from water. In the cold the chlorine reacts with the alkaline solution to form sodium hypochlorite. Some shaking facilitates the mixing of the chlorine with the NaOH formed. The solution coming out is a mixture of NaOCl and NaCl. The solution is cooled to about − 10°C when NaOCl crystallises.

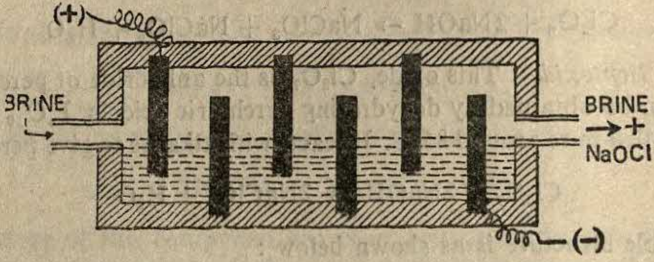


Fig. 21.3. Preparation of sodium hypochlorite

$$H_2O \rightarrow H^+ + OH^- ; \qquad NaCl \rightarrow Na^+ + Cl^-$$

at the cathode : $2H^+ + 2e \rightarrow H_2$ $\quad$ $2NaOH + Cl_2$

$$\downarrow$$

at the anode : $2Cl^- \rightarrow Cl_2 + 2e$ $\quad$ $NaOCl + NaCl + H_2O$

Oxidising properties : The following few sample reactions will establish sodium hypochlorite as a good oxidising agent :

$$2Fe(OH)_3 + 3NaOCl + 4NaOH \rightarrow 2Na_2FeO_4 + 3NaCl + 5H_2O$$

$$Ag_2O + NaOCl \rightarrow 2AgO + NaCl$$

$$2Cr(OH)_3 + 3NaOCl + 4NaOH \rightarrow 2Na_2CrO_4 + 3NaCl + 5H_2O$$

$$NaOCl + 2KI + 2HCl \rightarrow NaCl + 2KCl + H_2O + I_2$$

Chlorous Acid : The acid exists in solution only. Its salt eg. sodium chlorite is obtained by the reaction of sodium peroxide and chlorine dioxide :

$$Na_2O_2 + 2ClO_2 \rightarrow 2NaClO_2 + O_2$$

Sodium chlorite is unstable to heat and decomposes to sodium chlorate and sodium chloride :

$$3NaClO_2 \rightarrow 2NaClO_3 + NaCl$$

A solution of the free acid may be had by the reaction of H_2O_2 and ClO_2 :

$$H_2O_2 + 2ClO_2 \rightarrow 2HClO_2 + O_2$$

A study of the acid dissociation constant of $HClO_2$ and HClO proves the point that on increasing the oxidation number acid strength also increases :

$$K_A : HClO_2, \sim 10^{-2} ; HClO, \sim 10^{-8}.$$

Chloric Acid : We have seen that sodium hypochlorite is produced by the electrolysis of aqueous NaCl in the cold. If the same electrolysis is carried out at about 75°C sodium chlorate is produced. Potassium chlorate is also obtained similarly. The potassium hypochlorite formed initially changes to the chlorate :

$$3KOCl \rightarrow KClO_3 + 2KCl$$

Chlorate is also formed on the passage of chlorine through alkali solution in hot condition :

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$

$$3NaOCl \rightarrow NaClO_3 + 2NaCl$$

Chlorates decompose, on strong heating, to the chloride and oxygen :

$$2KClO_3 \rightarrow 2KCl + 3O_2 \ ; \ 4KClO_3 \xrightarrow{360°C} 3KClO_4 + KCl \ ; \ KClO_4 \xrightarrow{600°C} KCl + 2O_2.$$

Chlorates are oxidising agent and often cause explosion :

$$2KClO_3 + 4HCl \rightarrow 2KCl + Cl_2 + 2ClO_2 + 2H_2O$$

Chlorates are used in fireworks, in explosives and in match industry.

Perchloric Acid : Electrolytic oxidation of sodium chlorate gives perchlorate :

$$NaClO_3 \rightarrow Na^+ + ClO_3^- \ ; \ H_2O \rightarrow H^+ + OH^-$$

at the cathode : $2H^+ + 2e \rightarrow H_2$

at the anode : $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e$

$$ClO_3^- + \frac{1}{2}O_2 \rightarrow ClO_4^-$$

On the addition of KCl to the solution obtained after electrolysis the sparingly soluble $KClO_4$ crystallises. The potassium salt is mixed with H_2SO_4 and the mixture distilled when $HClO_4$ is obtained as the distillate. The acid may crystallise with one or more H_2O molecules. This is one of the strongest acids known. It usually fumes in air. The commercial variety is commonly 20% in strength. Concentrated $HClO_4$ often acts as an oxidant. However sometimes heating with concentrated acid may cause explosion. $NaClO_4$ can precipitate potassium ion from its solution as insoluble $KClO_4$. Potassium can be estimated gravimetrically as $KClO_4$.

The perchlorate ion is tetrahedral.

21.6. PREPARATION OF CHLORINE

21.6.1. Industrial preparation : Several methods are available for the purpose. Almost half of the world's requirement of chlorine comes from the electrolytic methods. Given below is a short resume of the different methods.

1. *Electrolysis of fused NaCl* : During the extraction of sodium from fused NaCl chlorine is obtained at the anode as an important by product (Chapter 15). The method goes by the name of Downs.

2. *Electrolysis of Brine according to Nelson's method* : During the manufacture of NaOH from brine, brine is electrolysed in a U shaped cell containing the electrolyte. The U shaped steel vessel serves as the cathode while a stout graphite rod positioned at the centre of the cell acts as the anode. Chlorine is given off at the graphite anode.

3. Spain is very rich in pyrolusite ore. This ore is reacted with concentrated HCl when chlorine is given off. Air is bubbled through the resulting liquid mass to recover the chlorine entirely :

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$

The $MnCl_2$ may be treated with lime when $Mn(OH)_2$ is formed in the first step. On aeration MnO_2 is obtained which can be reused :

$$MnCl_2 + Ca(OH)_2 \rightarrow Mn(OH)_2 + CaCl_2$$
$$Mn(OH)_2 + Ca(OH)_2 + \tfrac{1}{2}O_2 \rightarrow CaO.MnO_2 + 2H_2O$$

4. *Deacon's Process* : HCl gas can be oxidised to give chlorine by heating a mixture of HCl gas and air at 400-450°C in the presence of cupric chloride. The reaction is exothermic :

$$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2 + 28KCal \text{ (exothermic)}$$

The HCl is obtained by heating a mixture of NaCl and H_2SO_4. The mixture of HCl gas and air is preheated in a chamber to about 200°C. This heated mixture is then led into the catalyst chamber. The catalyst chamber contains pieces of burnt clay and $CuCl_2$. The purity of chlorine obtained by this method is not very high. This is mostly used in the manufacture of bleaching powder.

Laboratory Methods : For small quantity of chlorine any of the following reactions may be utilised :

1. $MnO_2 + 4HCl \xrightarrow{heat} MnCl_2 + 2H_2O + Cl_2$
2. $2KMnO_4 + 16HCl \xrightarrow{heat} 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$
3. $Ca(OCl)Cl + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$
4. $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$
5. $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

Properties of Chlorine : It is a greenish yellow pungent smelling gas and is poisonous in nature. It is sparingly soluble in water. It attacks the mucous membrane and causes cough and cold. It readily reacts with many metals to form their chlorides. With many eg. with sodium, copper, antimony, etc. lot of heat and light is produced :

$$2Na + Cl_2 \rightarrow 2NaCl \quad ; \quad 2Fe + 3Cl_2 \rightarrow 2FeCl_3$$
$$2P + 3Cl_2 \rightarrow 2PCl_3 \quad ; \quad PCl_3 + Cl_2 \rightarrow PCl_5$$

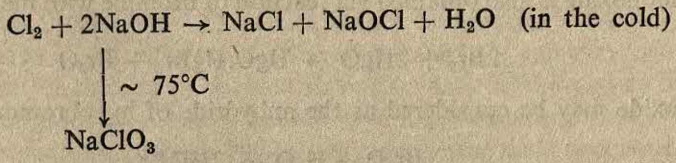
Oxidising reactions of chlorine are not restricted to the above reactions only. The following reactions with some compounds also speak for its strong oxidising nature :

$$SnCl_2 + Cl_2 \rightarrow SnCl_4 \text{ ; } H_2S + Cl_2 \rightarrow S + 2HCl$$
$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

It oxidises bromides and iodides to bromine and iodine respectively :

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2 \text{ ; } 2KI + Cl_2 \rightarrow 2KCl + I_2$$

Products of reaction with sodium hydroxide are dependent on the temperature :



$$\begin{array}{l} Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O \quad \text{(in the cold)} \\ \qquad \downarrow \sim 75^\circ C \\ \quad NaClO_3 \end{array}$$

Chlorine also functions as a decolouriser or a bleaching agent. It is believed that chlorine first reacts with water to produce oxygen which does the bleaching :

$$Cl_2 + H_2O \rightarrow 2HCl + \tfrac{1}{2}O_2$$

Uses of Chlorine : It is used in the manufacture of bleaching powder, in the manufacture of HCl, chlorates, perchlorates etc, and in paper industry.

21.7. COMPOUNDS OF BROMINE

21.7.1. Hydrogen Bromide and Hydrobromic Acid : The method of its synthesis is quite different from that of HCl. HCl is usually obtained by the reaction of NaCl and concentrated H_2SO_4. A similar procedure is not applicable to HBr because the liberated HBr is oxidised to bromine by the concentrated H_2SO_4 :

$$H_2SO_4 + 2HBr \rightarrow 2H_2O + SO_2 + Br_2$$

However reaction of a bromide salt with a weak acid produces HBr :

$$H_3PO_4 + KBr \rightarrow KH_2PO_4 + HBr$$

Commonly HBr is prepared by the reaction of red phosphorus and bromine :

$$2P + 3Br_2 \rightarrow 2PBr_3$$

$$PBr_3 + 3H_2O \rightarrow H_3PO_3 + 3HBr$$

$$5Br + P + 4H_2O \rightarrow H_3PO_4 + 5HBr$$

Red phosphorus and double its weight of water alongwith some sand are taken in a flask. The flask is provided with a dropping funnel and a delivery tube. The delivery tube is connected to a bulb containing some moist red phosphorus. On dropwise addition of bromine a vigorous reaction occurs among bromine, phosphorus and water (as shown in the above equations) and considerable heat is generated. The flask is therefore cooled in water. HBr alongwith some bromine pass out through the delivery tube. The bromine is converted to HBr in the bulb containing red phosphorus. Finally the HBr gas is collected over mercury. It may be absorbed in water to give hydrobromic acid ($H_3O^+Br^-$).

Hydrobromic acid is also a strong acid and is easily ionised in water. Many of the reactions of HBr are parallel to those of HCl. It should,however, be noted that bromides cannot react with H_2SO_4 to give HBr but get oxidised to bromine. It reacts with silver salts to precipitate AgBr. Whereas AgCl is readily soluble in ammonia, AgBr is less soluble.

21.7.2. Oxides of Bromine : *Bromine Monoxide* : Like chlorine monoxide, bromine monoxide is also obtained via reaction of bromine with mercuric oxide :

$$2Br_2 + 2HgO \rightarrow HgO.HgBr_2 + Br_2O$$

This oxide may be considered as the anhydride of hypobromous acid :

$$Br_2O + H_2O \rightarrow 2HOBr$$

Bromine oxide is stable and solid at a low temperature (~ − 40°C). It decomposes on heating :

$$2Br_2O \rightarrow 2Br_2 + O_2$$

Bromine Dioxide : This oxide, BrO_2, is obtained on the passage of electric discharge through a mixture of bromine and oxygen. It assumes solid state on cooling but decomposes on heating :

$$2BrO_2 \rightarrow Br_2 + 2O_2$$

21.7.3. Oxyacids of Bromine : Two oxyacids of bromine are well known : hypobromous acid, HBrO and bromic acid, $HBrO_3$. The oxidation number of bromine in these two oxyacids are + 1 and + 5 respectively.

Salts of hypobromous acid i.e. hypobromites are obtained by the reaction of bromine and alkali in the cold :

$$2NaOH + Br_2 \rightarrow NaBr + NaOBr + H_2O$$

On heating hypobromites are converted to bromates :

$$3NaOBr \rightarrow 2NaBr + NaBrO_3$$

Bromine reacts with hot KOH to give a mixture of KOBr and $KBrO_3$:

$$2KOH + Br_2 \rightarrow KOBr + KBr + H_2O$$

$$3KOBr \rightarrow KBrO_3 + 2KBr$$

Hypobromites function as oxidants as in solution we get bromine and oxygen:

$$4HOBr \rightarrow 2Br_2 + O_2 + 2H_2O$$

Bromates are superior oxidants than chlorates. Potassium bromate is used in a variety of quantitative volumetric analyses :

$$KBrO_3 + 5KBr + 6HCl \longrightarrow 3Br_2 + 3H_2O + 6KCl$$

$$KBrO_3 + 3H_3AsO_3 \xrightarrow{HCl} KBr + 3H_3AsO_4$$

$$2KBrO_3 + 3N_2H_4 \xrightarrow{HCl} 2KBr + 3N_2 + 6H_2O$$

$$2KBrO_3 + 2HCl + 5H_2S \longrightarrow Br_2 + 2KCl + 5S + 6H_2O$$

21.8. PREPARATION OF BROMINE

21.8.1. Industrial Preparation : The major source of bromine is sea water. Sea water is first made acidic with the addition of about 0.01 % sulphuric acid. Next requisite amount of chlorine is bubbled through, which is followed by air. The evolved bromine gas is absorbed in a solution of sodium carbonate when sodium bromide and bromate are formed. These salts are collected and again treated with acid. The liberated pure bromine is now cooled and collected in the liquid state :

$$2KBr + Cl_2 \rightarrow Br_2 + 2KCl$$

$$3Br_2 + 3Na_2CO_3 \rightarrow 5NaBr + NaBrO_3 + 3CO_2$$

$$5NaBr + NaBrO_3 + 6HCl \rightarrow 6NaCl + 3H_2O + 3Br_2$$

21.8.2. Laboratory Methods : On distilling a mixture of KBr, MnO_2 and sulphuric acid bromine is liberated. The bromine is led through cooled condensers and is collected in the liquid form :

$$2KBr + MnO_2 + 3H_2SO_4 \rightarrow MnSO_4 + 2KHSO_4 + Br_2 + 2H_2O$$

Properties : It is extremely corrosive in action. All kinds of handling of bromine has to be carefully done with rubber gloves and other precautionary measures. Its boiling point being rather low (59°C) it readily vapourises in open vessels. It is sparingly soluble in water. It reacts with many metals and non-metals :

$$2K + Br_2 \rightarrow 2KBr \ ; \ 2P + 3Br_2 \rightarrow 2PBr_3$$

Oxidising ability of bromine is less than that of chlorine but is still great enough :

$$H_2S + Br_2 \rightarrow S + 2HBr$$

$$2KI + Br_2 \rightarrow 2KBr + I_2$$

21.9. COMPOUNDS OF IODINE

21.9.1. Hydrogen Iodide and Hydroiodic Acid : HI cannot be obtained by the reaction of an iodide with concentrated H_2SO_4 because the HI is readily oxidised to iodine by the sulphuric acid :

$$2HI + H_2SO_4 \rightarrow I_2 + 2H_2O + SO_2$$

A method parallel to that of HBr is followed.

A mixture of iodine and red phosphorus is taken in a flask fitted with a dropping funnel and a delivery tube. The delivery tube is connected to a bulb containing moist red phosphorus. On dropwise addition of water HI and some I_2 are evolved. The mixture passes through the delivery tube and reacts further with the moist red phosphorus whereby the unreacted iodine is converted to HI. The HI gas is next led through a tube containing anhydrous calcium iodide to get dry HI. The gas may be dissolved out in water to get hydroiodic acid. The following reactions take place :

$$2P + 3I_2 \rightarrow 2PI_3 \ ; \ PI_3 + 3H_2O \rightarrow H_3PO_3 + 3HI$$

An alternative synthetic procedure involves a reaction between H_2S and iodine :

$$H_2S + I_2 \rightarrow 2HI + S$$

Properties : In the gaseous state HI is a covalent compound. In aqueous solution it forms the acid $H_3O^+I^-$. It is very highly soluble in water. The gas decomposes into the elements on heating :

$$2HI \rightleftharpoons H_2 + I_2$$

It is a very strong reducing agent and is itself oxidised to iodine :

$$O_2 + 4HI \rightarrow 2H_2O + 2I_2$$

$$H_2O_2 + 2HI \rightarrow 2H_2O + I_2$$

$$Cl_2 + 2HI \rightarrow 2HCl + I_2$$

$$H_2SO_4 + 6HI \rightarrow 4H_2O + S + 3I_2$$

$$H_2SO_4 + 2HI \rightarrow 2H_2O + SO_2 + I_2$$

$$H_2SO_4 + 8HI \rightarrow 4H_2O + H_2S + 4I_2 \text{ (in presence of excess HI)}$$

$$2FeCl_3 + 2HI \rightleftharpoons 2FeCl_2 + I_2 + 2HCl$$

$$2CuCl_2 + 4HI \rightarrow 4HCl + 2CuI + I_2$$

21.9.2. Potassium Iodide : This is the most important of the compounds. Two important methods are in use for its preparation :

1. Iodine is first reacted with hot concentrated KOH solution. The reaction product consisting of KI and KIO_3 is taken to dryness. This mixture is then heated with charcoal to reduce the iodate. Finally the iodide is recovered by crystallisation from water :

$$3I_2 + 6KOH \rightarrow 5KI + KIO_3 + 3H_2O$$

$$2KIO_3 + 3C \rightarrow 2KI + 3CO_2$$

2. Iron filings, iodine and water are reacted together to get FeI_2. After filtration the solution is treated with K_2CO_3 when $FeCO_3$ precipitates out and KI is retained in solution :

$$Fe + I_2 \rightarrow FeI_2$$

$$FeI_2 + K_2CO_3 \rightarrow FeCO_3 + 2KI$$

The ferrous carbonate is removed by filtration and the solution concentrated to recover KI. This is of vital importance as a chemical for iodometric determination of copper (II), iron (III), chromium (III) etc. (Chapter 29).

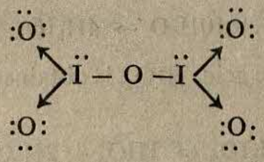
21.9.3. Oxides of Iodine : Several oxides are claimed : I_2O_4, I_4O_9, I_2O_5. Of these the iodine pentoxide, I_2O_5, is the most important. It may be considered as the anhydride of iodic acid HIO_3. Iodic acid may be heated to get this oxide at 240°C :

$$2HIO_3 \rightarrow I_2O_5 + H_2O$$

It is a colourless solid compound. It is the stablest of all the oxides of the four halogens. It can oxidise H_2S, HCl and CO to sulphur, chlorine and carbon dioxide while it is itself reduced to iodine :

$$5CO + I_2O_5 \rightarrow I_2 + 5CO_2$$

Its structure may be represented as shown below :



21.9.4. Oxyacids of Iodine : These are : HIO, HIO_3, HIO_4 and H_5IO_6.

Hypoiodous Acid: This acid, HIO, may be obtained in solution only. In the presence of alkalies hypoiodites are produced. Its synthetic methods are parallel to those of hypochlorous acid :

$$2I_2 + H_2O + 2HgO \rightarrow HgO.HgI_2 + 2HIO$$
$$I_2 + 2KOH \rightarrow KI + KIO + H_2O$$

Iodic Acid : This acid, HIO_3, is produced when fuming nitric acid and iodine (in the ratio 10 : 1) are boiled. The excess nitric acid is removed at about 200°C and the remaining material is crystallised from hot water to get HIO_3 :

$$3I_2 + 10HNO_3 \rightarrow 6HIO_3 + 10NO + 2H_2O$$

The acid may also be produced by agitating a suspension of iodine in water by chlorine :

$$I_2 + 5Cl_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$$

Potassium iodate is sparingly soluble in water. Hence this salt may be easily prepared by reacting hot KOH solution with iodine :

$$3I_2 + 6KOH \rightarrow KIO_3 + 5KI + 3H_2O$$

Potassium iodate is a good oxidant. Given below are a few examples :

$$2KIO_3 + 5H_3AsO_3 + 2HCl \rightarrow I_2 + 5H_3AsO_4 + 2KCl + H_2O$$
$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O$$
$$2HIO_3 + 5H_2S \rightarrow I_2 + 6H_2O + 5S$$

Potassium Biiodate : This salt is produced on crystallisation of a solution of KIO_3 and HIO_3 in 1 : 1 ratio. This is also obtained by reacting barium iodate suspension with potassium bisulphate. The insoluble barium sulphate is removed and the filtrate on concentration gives crystals of $KH(IO_3)_2$:

$$Ba(IO_3)_2 + KHSO_4 \rightarrow BaSO_4 \downarrow + KH(IO_3)_2$$

It is an excellent primary acidimetric standard.

Periodic Acid : The acid may assume several formulas although in all cases the oxidation number of iodine is + 7. Disodium paraperiodate, $Na_2H_3IO_6$, crystallises as a sparingly soluble product when a boiling suspension of iodine in strongly alkaline medium is oxidised by a stream of chlorine :

$$18NaOH + I_2 + 7Cl_2 \rightarrow 2Na_2H_3IO_6 + 14NaCl + 6H_2O$$

Reaction of $AgNO_3$ and $Na_2H_3IO_6$ in solution gives Ag_5IO_6. This latter compound is next treated with chlorine in aqueous medium. The precipitated AgCl is removed and periodic acid, H_5IO_6, is recovered :

$$4Ag_5IO_6 + 10Cl_2 + 10H_2O \rightarrow 4H_5IO_6 + 20AgCl + 5O_2$$

Another form of periodic acid, HIO_4, is obtained on heating H_5IO_6 at 100°C under vacuum :

$$H_5IO_6 \rightarrow HIO_4 + 2H_2O$$

Periodic acid is a good oxidant as is shown by the following reactions :

$$2MnSO_4 + 5H_5IO_6 \rightarrow 2HMnO_4 + 5HIO_3 + 2H_2SO_4 + 7H_2O$$

$$KIO_3 + 7KI + 8HCl \rightarrow 8KCl + 4I_2 + 4H_2O$$

21.10. CATIONIC PROPERTIES OF IODINE

All throughout our discussion on the chemistry of the elements in the different groups we have made the important observation that more and more of metallic properties appear in the elements with increasing atomic number in a particular group. Although iodine is mainly a non-metal some metallic properties do appear in this element because of increase in its atomic number. Similar metallic properties are less pronounced in bromine.

Monopositive Iodine : Silver nitrate and iodine react with pyridine in chloroform medium to give the cationic iodine compound $[I(C_5H_5N)_2]NO_3$:

$$AgNO_3 + I_2 + 2py \rightarrow AgI + [I(py)_2]NO_3 \quad (py = C_5H_5N)$$

The precipitate of AgI is filtered off and the filtrate treated with ether to precipitate crystals of $[I(py)_2]NO_3$. This is a complex compound of monovalent iodine. Iodine (I) has a coordination number two in this complex. Pyridine functions as the monodentate coordinating ligand linking to iodine (I) through the heterocyclic nitrogen lone pair. That iodine is indeed cationic is proved from the following experiments:

1. On electrolysis of this compound in chloroform iodine is observed to be liberated at the cathode : $2I^+ + 2e \rightarrow I_2$

2. The compound reacts with iodide ion and liberate iodine :

$$I^+ + I^- \rightarrow I_2$$

The liberated iodine can be titrated with sodium thiosulphate.

Tripositive Iodine : Fuming nitric acid and iodine react in presence of acetic anhydride to give iodine triacetate. On electrolysis of this compound with silver cathode one gram mole of AgI is formed at the cathode for every *Faraday* of electricity :

$$I(CH_3COO)_3 \rightleftharpoons I^{3+} + 3CH_3COO^-$$

at the cathode : $I^{3+} + 3e \rightarrow \frac{1}{2}I_2$; $Ag + \frac{1}{2}I_2 \rightarrow AgI$

The compound reacts with iodide ion according to the following reaction :

$$I^{3+} + 3I^- \rightarrow 2I_2$$

21.11. PREPARATION OF IODINE

Iodine is usually recovered from two sources : (1) Chile saltpetre and (2) sea weeds.

1. *From Chile saltpetre* : Chile saltpetre is basically $NaNO_3$. This carries alongwith it some small amount of sodium iodate. On crystallisation of this saltpetre from water the first fractions contain $NaNO_3$. Mother liquor contains the sodium iodate $NaIO_3$. The mother liquor is reacted with sodium bisulphite when iodine is precipitated :

$$2NaIO_3 + 5NaHSO_3 \rightarrow I_2 + 3NaHSO_4 + 2Na_2SO_4 + H_2O$$

The precipitated iodine is collected and purified via sublimation.

2. *From sea weeds* : There are some sea weeds which absorb iodine from sea water probably in the form of iodide. On burning these weeds an ash is left. This ash contains about 0.5 % iodine as sodium and potassium salts. This ash is agitated with water and the solution is concentrated and allowed to crystallise. Potassium sulphate, potassium chloride and sodium chloride crystallise out first. The mother liquor from this filtration contains small amounts of iodides, bromides and sulphides. This mother liquor is treated with sulphuric acid when sulphides decompose to give H_2S. Thereafter the solution is distilled with MnO_2 and H_2SO_4. The liberated iodine vapour is condensed into a series of stoneware bottles known as *aludels*. Iodine collected in these aludels is purified by sublimation.

Laboratory Method : Besides the above two industrial scale preparations small quantities of iodine can be obtained by the reaction of KI with MnO_2 and concentrated H_2SO_4. On heating deep violet vapour of iodine is given off. This is cooled and collected as almost black looking iodine crystals :

$$2KI + MnO_2 + 3H_2SO_4 \rightarrow I_2 + 2KHSO_4 + MnSO_4 + 2H_2O$$

Properties. It is easily sublimable solid. In the solid crystalline state it looks almost black-violet. It is sparingly soluble in water but dissolves readily in presence of KI due to the formation of potassium triiodide, KI_3. The solution assumes a blood-red colour. Iodine is readily soluble in alcohols, carbon disulphide, carbon tetrachloride. The colour in the alcoholic solvents is red while that in others is distinct violet typical of the colour of iodine vapour.

It reacts with several elements but at a slower rate than chlorine or bromine.

$$2P + 3I_2 \rightarrow 2PI_3$$

$$2Na + I_2 \rightarrow 2NaI \; ; \; Hg + I_2 \rightarrow HgI_2$$

Its oxidising power is less than the other halogens. However it can oxidise sulphite to sulphate, arsenite to arsenate, H_2S to sulphur, thiosulphate to tetrathionate etc :

$$I_2 + H_2S \rightarrow 2HI + S \;;\; Na_2SO_3 + I_2 + H_2O \rightarrow Na_2SO_4 + 2HI$$

$$Na_3AsO_3 + I_2 + H_2O \rightarrow Na_3AsO_4 + 2HI$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

In alkaline solution we get either hypoiodite or iodate depending on the reaction temperature :

$$I_2 + 2NaOH \rightarrow NaOI + NaI + H_2O \quad \text{(dilute NaOH ; in the cold)}$$

$$3I_2 + 6NaOH \rightarrow NaIO_3 + 5NaI + 3H_2O \quad \text{(conc. NaOH ; in hot solution)}$$

Uses : It is used in pharmacy at *tincture of iodine* (10% solution of iodine in alcohol). It finds use as an important laboratory chemical and in the syntheses of various organic derivatives, dyes, etc.

EXERCISES

1. The halogens form a very cohrent group in the entire periodic table. Justify this statement.

2. Halogens are the most electronegative elements and their electron affinities are also high. Do you expect any metallic property to appear in any of these elements? Justify your answer.

3. Fluorine has certain characteristics which are different from the other members of the group. Enumerate these specialities and offer an explanation for such behaviour.

4. Complete the following reactions :

(*a*) $Fe(OH)_3 + NaOCl + NaOH \rightarrow$
(*b*) $KClO_3 + HCl \rightarrow$
(*c*) $KMnO_4 + HCl \rightarrow$
(*d*) $KBr + H_2SO_4 \rightarrow$
(*e*) $KBrO_3 + KBr + HCl \rightarrow$
(*f*) $Br_2 + Na_2CO_3 \rightarrow$
(*g*) $I_2 + Cl_2 + H_2O \rightarrow$
(*h*) $KIO_4 + KI + HCl \rightarrow$
(*i*) $KI + MnO_2 + H_2SO_4 \rightarrow$

5. What are the difficulties encountered in the preparation of fluorine? Give a description of the currently used method.

6. Describe the preparation, properties and uses of the following compounds :

(*a*) potassium iodide (*b*) potassium bromate (*c*) hydroiodic acid (*d*) potassium perchlorate (*e*) potassium chlorate

7. Give a description of the products obtained out of electrolysis of NaOH solution under different conditions.

8. Discuss the electronic structure of the following compounds :

(*a*) Cl_2O (*b*) ClO_2 (*c*) Cl_2O_7 (*d*) HCl gas and HCl acid

9. Give the description of the industrial preparation of hydrochloric acid. Describe some of its reactions and uses.

CHAPTER 22

THE NOBLE GASES

22.1. INTRODUCTION

Scientific developments have not followed any regular predetermined course. Most often outstanding and challenging experiments have been conducted by great experimentalists. Equally brilliant theoreticians have appeared later on the scene to explain the findings of the experimentalists. Sometimes however gifted theoreticians have brought in exciting new theories, the proofs of which have been provided by top class experimentalists at a later date. So we see sometimes experiments preceded theories and at some other times experiments followed theories. This is how humanity has benefited in the long run.

An in-depth look into the history of scientific growth provides a startling fact that many great experimental findings had not received due recongnition or explanation at the time these experiments were performed. One such case relates to the great experiment conducted by Henry Cavendish in 1785 in which was hidden the clue to the discovery of the noble gases. However the beauty of the experiment conducted by Cavendish was that it stood the test of time over a period extending more than a century. It does great credit to him when Ramsay and Rayleigh in 1894 looked into his experiment of 1785 and found that it was too fine to be erroneous and it was in this great experiment of Cavendish that these two later luminaries discovered most of the noble gases.

22.2. THE DISCOVERY OF THE NOBLE GASES

In 1785 Henry Cavendish was engaged in some fundamental research concerning composition of air. In an inverted big sized flask he introduced air and excess oxygen. Inside the flask he had an arrangement for causing spark between two platinum wires. On sparking the nitrogen combined with oxygen to form N_2O_5. This oxide was absorbed by strong KOH solution. Repeated sparking and treatment with KOH removed all the nitrogen of the air. The remaining excess oxygen was absorbed in potassium pentasulphide. But Cavendish was taken aback when he found that he could not get the entire amount of the remaining gas dissolved out by treatment with pentasulphide nor repeated sparking with fresh oxygen was of any avail. He made sure that he was right. He therefore concluded that air which is mostly composed of oxygen and nitrogen must be carrying some constituents which refused to combine with oxygen under the condition of sparking and that this volume is 1/120th part of air. This was a great experiment by the standard prevailing in 1785 but the generations of chemists coming after Cavendish had shown little interest in his experiment. Fortunately for us Ramsay and Rayleigh got interested in precise determination of the density of nitrogen and it was then that Henry Cavendish's experiment appeared before them in its full glory and mysticism.

Ramsay and Rayleigh got interested in getting precise density data on nitrogen. In 1894 they selected for their purpose two different sources of nitrogen : (*a*) nitrogen of the atmosphere and (*b*) nitrogen from thermal decomposition of ammonium nitrite : $NH_4NO_2 \rightarrow N_2 + 2H_2O$. Air had to be got rid of oxygen and carbon dioxide. This they acheived by passing air over red hot copper when oxygen was trapped as CuO. The issuing gas was then led through concentrated KOH solution to get the CO_2 absorbed. The gas remaining was taken to be pure nitrogen and its density was determined. It was found that 1 litre of this 'nitrogen' weighed 1.2572 gram. On the contrary 1 litre of nitrogen prepared from ammonium nitrite weighed 1.2505 gram. Ramsay and Rayleigh, being chemists of a very high order, could recognise that these two sources of nitrogen provided two varieties which had a genuine difference in their density and that this difference could not be passed off as experimental error. The inevitable conclusion that they arrived at was that nitrogen of the atmosphere must be carrying some other gaseous constituents whose average density was higher than that of pure nitrogen obtained from a genuine chemical source. Now a search of the literature revealed that long back the great Henry Cavendish had performed a remarkable experiment that demostrated that air had certain constituents other than nitrogen which defied all attempts to make them combine with oxygen under sparking. Now Ramsay and Rayleigh got the clue from an outstanding experimentalist of the by-gone era. The question now was : what this 1/120th part of air did contain? Was there a single element or more? Research now became more demanding and exacting. They realised it was time to break new ground and that they really did in 1895 onwards.

Ramsay and Rayleigh passed air through a tube containing copper at red heat and then over hot magnesium. This was done repeatedly to get rid of oxygen and nitrogen :

$$2Cu + O_2 \rightarrow 2CuO \quad ; \quad 3Mg + N_2 \rightarrow Mg_3N_2$$

Thereafter carbon dioxide and moisture were removed by the use of lime and phosphorus pentoxide. The atomic/molecular weight of the remaining gas was determined and was found to be 40. This gas was found extremely inert. This gas did not undergo any reaction with hot metals, red hot copper oxide, KOH, $KMnO_4$, Na_2O_2 etc. It did not react with fluorine even. Because of the extreme inertness of the gas Ramsay called it argon (meaning lazy in Greek).

Originally Ramsay used hot magnesium to remove nitrogen. The reaction is somewhat slow. A better method is to pass air through an iron retort containing 90% CaC_2 and 10% $CaCl_2$ at 800°C. Calcium cyanamide and carbon dioxide alongwith a small amount of CO are formed.

$$CaC_2 + N_2 \rightarrow CaN.CN + C \quad ; \quad C + O_2 \rightarrow CO_2$$

The little CO formed is removed by passing the issuing gas through a tube containing CuO at red heat and then the CO_2 formed is absorbed by KOH :

$$CO + CuO \rightarrow Cu + CO_2 \; ; \; CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$$

The water is absorbed in conc. H_2SO_4. The gas now contains mostly argon.

After the discovery of argon Ramsay started to look for argon in different minerals. In the uranium bearing mineral cleivite he found a gas whose spectrum appeared to match with that of the outer atmosphere of the sun. This gas he named helium (meaning sun in Greek). Most of the hot springs all over the world contain about 5% helium. Natural gas also contains about 0.9% helium. In Chapter 2 we have described how Rutherford established the identity of alpha particles with doubly charged helium ions. The vapour density of helium was establshed as 2 while the atomic weight worked out to be 4.0. Note that the noble gases are all monoatomic in nature so that their molecular weight is the atomic weight.

After the discovery of helium and argon Ramsay naturally turned to the question of their positions in the periodic table. He had to introduce a zero group in the periodic table after group VIII for the noble gases. After having placed helium after hydrogen and argon after chlorine Ramsay sensed there appears to be missing another noble gas after fluorine. He could come to these conclusions on the basis of the atomic weights of the two gases helium and argon. It therefore occurred to him that the gas he was considering to be argon may not be 100% pure argon and that this may carry some amount of the other noble gas that has eluded him. The obvious experiment that suggested itself was to see if fractional distillation of liquid argon gives any element other than argon. Then Ramsay and Travers started fractional distillation of as much as 18 litres of liquid argon. Gases were collected at different temperatures. The gas collected at the lowest temperature gave a spectrum which was found to be entirely new. This gas was again liquefied and then fractionally distilled again and thus a pure specimen of a new gas, called neon, was collected. The atomic weight of this gas was found to be 20 from its vapour density 10.1.

The heavier fractions collected from fractional distillation of 30 litres of liquid argon provided two more new noble gases called krypton and xenon. Their atomic weights were found to be about 84 and 131 respectively.

It is now known with certainty that out of 100 litres of air the volumes of the noble gases are : argon 934 ml, neon 1.82 ml, helium 0.52 ml, krypton 0.114 ml. and xenon 0.009 ml. Thus the total volume of the noble gases works out to be about 1/120th part of air. This is exactly the volume of gas which refused to combine with excess oxygen under conditions of sparking. Thus Henry Cavendish passed the acid test of a great experimentalist of his time. Cambridge University has reasonably honoured this fine chemist by naming one of their laboratories after him. Ramsay was honoured with the Nobel award for chemistry in 1904.

22.3. PREPARATION OF THE NOBLE GASES

The following steps are carried out : 1. Fractional distillation of liquid air is utilised in their isolation. The boiling points of the different constituents of air are as given below :

Element :	N_2	O_2	He	Ne	Ar	Kr	Xe
B.P.(°C) :	−196	−183	−269	−246	−187	−152	−109
B.P.(°K) :	77	90	4	27	86	121	164

A scrutiny of the above boiling points indicates that on fractional distillation argon, krypton and xenon are likely to accompany oxygen while helium and neon will go alongwith nitrogen.

2. On further fractional distillation of liquid oxygen a fraction rich in krypton and xenon and another fraction rich in the lighter argon can be separated. However both these fractions will also have oxygen as contaminant. Repeated fractionation will provide purer varieties of these noble gases.

3. Helium and neon are found in the nitrogen fraction of the liquid air. The gaseous mixture containing nitrogen, helium and neon is passed over heated calcium and nitrogen is trapped as calcium cyanamide. The gaseous mixture now consisting of helium and neon is cooled by liquid hydrogen (B.P. – 253°C) when neon turns into the liquid form. Helium can be recovered as a pure gas. Liquid neon afterwards may be warmed upto the gaseous form.

22.4. A STUDY OF THE CHEMISTRY OF THE NOBLE GASES

This family of gases earlier was called as inert gases or rare gases because of their extreme inertness towards chemical reactions. Since the middle sixties several compounds of xenon and to a limited extent of krypton have been established. Because of these findings they are nowadays known as noble gases.

The electron distribution of helium shows that it has a saturated electronic shell, namely $1s^2$. For the rest of the noble gases the outer levels have the very stable octet combination : s^2p^6. That these electronic configurations of the noble gases lend an extra stability to the system is revealed by an inspection of the reactivity of the alkalies and the halogens in respect of their electron distribution. The alkalies have one electron more than the preceding noble gas and thus readily forms monopositive cations. On the other hand the halogens have one electron less than the following noble gas and hence tend to attain the noble gas electronic configuration either by gaining one more electron (forming halide ions) or by sharing one more electron with a suitable partner forming a shared pair covalent bond. Thus the noble gases serve as a bridge between the highly electropositive alkalies and the highly electronegative halogens.

At the time of Mendeleev not a single noble gas was discovered. So his periodic table did not provide for these elements. From the standpoint of electron distribution, with the exception of helium, the noble gases have eight electrons in their outermost quantum shell. Hence they should naturally be members of Group VIII of the periodic table. But then Mendeleev had already allotted this group to the iron triad, ruthenium triad and the osmium triad. Ramsay therefore introduced the zero group coming after the eighth group in the periodic table. The zero group had the significance that the chemical reactivity of these elements was almost next to nothing. It was assumed that their combining capacity was almost zero. Table 22.1 records some of the characteristics of these elements.

Table 22.1. A Comparative Study of the Noble Gases

Element	Atomic Number	Electron Distribution	First Ionisation Potential (*ev*)	Boiling Point (°K)
He	2	$1s^2$	24.58	4
Ne	10	$[He]2s^22p^6$	21.56	27
Ar	18	$[Ne]3s^23p^6$	15.75	86
Kr	36	$[Ar]3d^{10}4s^24p^6$	13.99	121
Xe	54	$[Kr]4d^{10}5s^25p^6$	12.13	164

By virtue of their having a very stable outer electronic shell these elements normally cannot lose any electron nor can gain any. Hence they remain as monatomic gases. We have already observed in Chapter 5 that the condition for the formation of a diatomic molecule is that each of the atoms must have one unpaired electron. This condition just does not prevail in the noble gases. Hence they remain in the monatomic form.

As in the case of other elements here too we find that there is a decrease in the ionisation potential of the noble gases with increasing atomic number. Linus Pauling predicted for the first time that if at all there be discovered any compound of these elements xenon stands the best chance because of its lowest first ionisation potential. This forecast proved to be true when in the mid sixties and afterwards several xenon compounds XeF_2, XeF_4, XeF_6 were obtained by interacting xenon with fluorine. Some of these compounds were further reacted with SiO_2 and still newer types of compounds $XeOF_4$, XeO_3, H_4XeO_6 were isolated. Some similar compounds of krypton like KrF_2, KrF_4, H_2KrO_4 have also been reported. Outlines of the syntheses of some of the compounds are given below :

$$\underset{(1\text{part})}{Xe} + \underset{(5\text{ parts})}{F_2} \xrightarrow[\text{under pressure in a nickel bulb}]{400°C} \underset{\substack{\text{(colourless}\\\text{crystals)}}}{XeF_4}$$

$$\underset{(1\text{ part})}{Xe} + \underset{(1\text{-}20\text{ parts})}{F_2} \xrightarrow[\text{200 atmosphere pressure}]{300-700°C} \underset{\substack{\text{(colourles}\\\text{crystals)}}}{XeF_6}$$

$$\begin{tikzcd}
2XeF_6 + SiO_2 \arrow[r, "\sim 50°C"] & \underset{\substack{\text{(colourless}\\\text{liquid)}}}{2XeOF_4 + SiF_4} \arrow[d, "+ SiO_2"] \\
\underset{\substack{\text{(colourless}\\\text{crystals)}}}{2XeO_3 + SiF_4} & 2XeO_2F_2 + SiF_4 \arrow[l, "+ SiO_2"']
\end{tikzcd}$$

Uses : Neon is usually a non-conductor. But it conducts electricity at 10-20 mm pressure and under 200 volts. Under these conditions neon gives a beautiful red spectrum which is used in advertisements. Different attracting colours are produced when neon is introduced under low pressure in glass tubes of varying shapes and colours and a suitable voltage is applied. These are usually called neon sign tubes.

Earlier electrical filament bulbs used to be filled with nitrogen in order to save the tungsten filament from decay via formation of oxide in presence of air. Nowadays the bulbs are filled with argon which adds to the longivity of the tungsten wire. Krypton and xenon are also used inside the electric bulbs. These run better than argon filled bulbs.

Helium is nowadays being used for scientific researches at very low temperatures (B.P. 4°K). For divers a mixture of oxygen and helium (as a diluent) is used for inhaling while working under high pressure. If ordinary water is used it is found that deep into the water under heavy pressure some of the nitrogen gets dissolved into the blood stream. After the divers come back on to the surface at ordinary pressure the dissolved nitrogen is given out and this causes severe pain. Helium however is not soluble in blood even under high pressure.

EXERCISES

1. Name and give the electron distributions of the noble gases. Explain the general chemical inactivity of these elements.
2. Fluorine is diatomic while neon is monatomic. Explain.
3. Give in outline the syntheses of a few compounds of noble gases.
4. Mention some uses of the noble gases. How do you justify their position in the periodic table?

CHAPTER 23

SOME TRANSITION ELEMENTS

23.1. INTRODUCTION

In inorganic chemistry the transition elements occupy a place of pride. Much of the ideas of coordination chemistry and valence theories as also magnetochemistry have developed around this class of compounds. In this elementary text we shall attempt to present the chemistry of a few selected transition elements of the first series. These elements are chromium, manganese, iron, cobalt and nickel. The chemistry of another first series transition element, namely copper, will be taken up in the next Chapter along with silver and gold. But before we proceed to discuss the chemistry of these elements individually it will only be fair to give a resume of transition elements versus representative elements.

23.2. TRANSITION ELEMENTS VERSUS REPRESENTATIVE ELEMENTS

In Chapter 1 we have presented the definitions of these two classes of elements. Representative elements are those elements which have either no electrons in their *d* orbitals or that their *d* orbitals are completely filled in their ground states or in any of their oxidation states. Thus representative elements have electrons in their outermost *s* or *p* orbitals. On the contrary transition elements are those elements which have incompletely filled *d* shells in their ground states or in any of their oxidation states. The electron distributions of the two elements sulphur and chromium belonging to sub-groups VIB and VIA respectively are given below :

Element	*Atomic Number*	*Electron Distribution*
Sulphur	16	$[Ne]3s^23p^4$
Chromium	24	$[Ar]3d^54s^1$

Thus we watch that there is no *d* electron in sulphur while in chromium there are only 5 electrons in the $3d$ levels which can accommodate as many as ten electrons. Thus sulphur is regarded as a representative element while chromium is classed as a transition element. Similarly chlorine of atomic number 17 has the electron distribution $[Ne]3s^23p^5$ while manganese of atomic number 27 has the electronic configuration $[Ar]3d^54s^2$. Thus manganese also has an incompletely filled $3d$ level and hence goes to the family of transition elements. As we shall see later on in many of the different oxidation states of the transition elements the *d* level remains incompletely filled.

We now enumerate some of the distinctions in the chemical properties of these two classes of elements.

1. In a series of transition elements with increasing atomic number electrons are added to the penultimate *d* level. For representative elements, on the other hand, with increasing atomic number electrons are added to the outer *s* or *p* levels.

2. In a series of representative elements electrons are added to the *s* or *p* level of the same quantum number. As these orbitals take on more and more of electrons the nucleus also takes on more and more of protons. The result is a decrease in size of the atoms along a given series of the periodic table. Because of the gradual decrease in size ionisation potential and electronegativity of the elements continue to increase with increasing atomic number :

Element	Li	Be	B	C	N	O	F
Atomic radius (A)	1.52	1.11	0.88	0.77	0.70	0.66	0.64
I.P. (*ev*)	5.39	9.32	8.29	11.25	14.53	13.61	17.42
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0

In the case of the transition elements of the first series electrons are added to the penultimate 3*d* shell just below the 4*s* outer level. Here also there is a decrease in atomic size with increasing atomic number but that this decrease is less pronounced compared to that in a series of representative elements : Ionisation potential and electronegativity also decrease quite slowly :

Element	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Atomic radius (A)	1.47	1.34	1.27	1.26	1.26	1.26	1.25	1.28
I.P. (*ev*)	6.82	6.74	6.76	7.43	7.90	7.86	7.63	7.72
Electronegativity	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9

3. There is an important difference in valences shown by these two classes of elements. The representative elements usually (not always) exhibit valence corresponding to the group to which they belong. However exceptions are found in some cases, particularly when there occurs an inert s^2 pair of electrons. In these cases valence varies by two units. Excellent examples are found in tin (II), tin (IV) ; lead (II), lead (IV). Sulphur also shows valences differing by two units : (II), (IV) and (VI).

But the variation of valence in transition metals is commonly a rule rather than an exception. Because of the slight difference in energies of the different *d* electrons it is possible to utilise varying number of electrons for valence purpose and this can be realised by reagents of different oxidising ability. The following examples convince us that in the family of transition elements a very wide variation of valences is a reality :

Element	*Oxidation numbers*							
chromium		*+6*	+5	+4	*+3*	+2	+1	0
manganese	*+7*	+6	+5	*+4*	*+3*	*+2*	+1	0
iron		+6		+4	*+3*	*+2*		0
cobalt					*+3*	*+2*	+1	0
nickel				+4	+3	*+2*	+1	0

Of the very many oxidation numbers the ones italicised are the most well known.

4. Coordination complexes are formed both by the representative elements and the transition elements but in the case of the transition elements complex formation is a dominating feature of their chemistry. During complexation there is a splitting of the *d* orbitals (Chapter 12) which leads to stability. Hence transition elements, which possess *d* electrons, are necessarily better poised to generate complexes than the representative elements. The latter elements have filled *s* or *p* orbitals which either cannot split (eg. the *s* orbital) or energy raised equally (eg. the three *p* orbitals placed along the three cartesian axes) in an octahedral geometry. Thus no special stability is gained by the representative elements.

5. In the representative elements the outer orbital electrons are placed in the *s* or *p* orbitals. As a result on excitation these electrons are lifted to orbitals of much higher energy. Therefore energy absorption takes place over a range higher than the energy of the visible range. Hence in most cases compounds of representative elements are practically colourless. Unless absorption occurs over the smaller energy visible range our eyes cannot distinguish any colour.

On the other hand the transition elements possess electrons in their *d* orbitals. These orbitals split during compound formation so that on excitation electrons from a lower energy *d* orbital move to other *d* orbitals of slightly different energy (Fig. 12.3). This absorption of energy is over a small range i.e. over the visible range and hence we see the compound coloured through the small energy transmitted light. This explains why transition metal compounds are so often coloured. Some examples are cited below :

compounds of representative elements	*colour*	*compounds of transition elements*	*colour*
sodium nitrate	colourless	bis(dimethylglyoximato) nickel (II)	rose-red
sodium sulphate	colourless	hexammine cobalt (III) chloride	orange
sodium aluminium sulphate	colourless	tetrammine copper (II) sulphate	deep blue

6. In general compounds of representative elements contain even number of electrons and as a consequence these turn out to be diamagnetic. Only in a few cases the molecules are of the odd electron type eg. NO, NO_2, ClO_2. In these cases they are per force paramagnetic. On the other hand transition element compounds can show wide range of valences having varying number of *d* electrons. Besides, in the same valence state depending on the stereochemistry the same metal ion may form compounds with paired spins or different number of unpaired spins. Thus paramagnetism and diamagnetism may both be found in compounds of transition elements. To cite an example the tetrahedral $NiCl_4^{2-}$ shows paramagnetism to the extent of two unpaired electrons while bis(dimethyl glyoximato) nickel (II) is diamagnetic. Note that both the compounds contain $3d^8$ nickel (II).

7. Many transition metal compounds are proven catalysts in a variety of industrial processes. It is believed that some unstable intermediates are formed

through the participation of the *d* orbitals. These intermediates lower the activation energy of a complex industrial process and brings about the reaction at a comparatively lower temperature and at a faster rate.

CHROMIUM

23.3. A RESUME OF THE CHEMISTRY OF CHROMIUM

Some important characteristics of chromium are collected in Table 22.1. Its electronic configuration identifies it as a transition element. The 3*d* orbitals are incompletely filled in its elementary state and in many of its ions of varying valence. Depending on the nature of the oxidants the element can show all the following valences : + 6, + 5, + 4, + 3, + 2, + 1 and 0. Compounds in all these states are well established. However of all these states hexavalent, trivalent and bivalent chromium are the best studied.

Table 22.1. Some Properties of Chromium

Element	Atomic Number	Electron Distribution	Ionisation Potential (*ev*)	Electro-negativity	Atomic Radius (A)	Ionic(M^{3+}) Radius (A)
Cr	24	[Ar]$3d^54s^1$	6.76 16.49 30.25	1.6	1.27	0.52

It is a general rule that as the valence (oxidation number) increases the oxidising ability increases and so does the acid character. On the other hand lower valences become reducing in nature and there occurs an increase in the basic character. Thus hexavalent chromium is oxidising in character while bivalent chromium is a good reducing agent.

Increase in valence i.e. in oxidation number makes the ion more electronegative. Hence higher valent oxides are acidic in nature. Conversely lower valent oxides are basic in nature. It follows therefore that intermediate valences will be amphoteric. Thus CrO_3 is entirely acidic and reacts with alkalies to give chromates (eg. Na_2CrO_4). Chromic hydroxide, $Cr(OH)_3$, is amphoteric. It gives chromic salts with acids (eg. $CrCl_3$) and chromites with alkalies (eg. $NaCrO_2$). Chromous hydroxide, $Cr(OH)_2$, is wholly basic. It gives chromous salts with acid (eg. $CrCl_2$).

The lower valent compounds are rather unstable and get easily oxidised in the presence of air. Because of air sensitivity all lower valent compounds are synthesised and handled in an inert atomosphere like nitrogen. Different oxidation states have different number of electrons. Depending on the nature of the compound, say the types of ligands in a complex, there will be different number of unpaired electrons. From a study of the magnetism of the compound it is possible to decide on the valence and the stereochemistry of the compound concerned.

23.3.1. Hexavalent Chromium : This valence of chromium is restricted to a few compounds only. These are chromic oxide, chromates, dichromates, chromyl chloride and peroxychromate.

Chromic Oxide (*Chromium Trioxide*) : This compound, CrO_3, is obtained as bright red crystals on treatment of potassium dichromate with H_2SO_4 :

$$K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + 2CrO_3 + H_2O$$

The crystals are filtered through a sintered glass funnel, washed with HNO_3 and finally dried in a stream of hot air. It is readily soluble in water and produces chromic acid H_2CrO_4. It reacts with alkalies to give chromates: Na_2CrO_4, K_2CrO_4 etc. It decomposes on heating to Cr_2O_3 and oxygen :

$$4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$$

It is a good and useful oxidant. It is used in oxidising many organic compounds :

$$2CrO_3 + 3SnCl_2 + 12HCl \rightarrow 2CrCl_3 + 3SnCl_4 + 6H_2O$$

$$2CrO_3 + 3H_2S + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3S + 6H_2O$$

$$3C_6H_5CHO + 2CrO_3 \rightarrow 3C_6H_5COOH + Cr_2O_3$$

Sodium/Potassium Dichromate : For large scale preparation chromite ore ($FeCr_2O_4 = FeO.Cr_2O_3$) is mixed with Na_2CO_3 or K_2CO_3 alongwith lime, $Ca(OH)_2$, and heated in a stream of air. The lime helps to keep the mixture porous to facilitate aeration :

$$4FeCr_2O_4 + 8Na_2CO_3(K_2CO_3) + 7O_2 \rightarrow 2Fe_2O_3 + 8Na_2CrO_4(K_2CrO_4) + 8CO_2$$

The reaction product is agitated with water and filtered to get rid of insoluble matter. The filtrate containing the chromate is acidified with H_2SO_4 when the dichromate is formed :

$$\underset{\text{(yellow)}}{2Na_2CrO_4} + H_2SO_4 \rightarrow \underset{\text{(Orange)}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

Addition of KCl to a solution of $Na_2Cr_2O_7$ forces crystallisation of the less soluble potassium dichromate :

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Addition of H^+ ion to the chromate ion changes it to the dichromate ion while addition of OH^- changes the dichromate to the chromate :

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

$$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^- + H_2O$$

In acidic medium potassium dichromate is a very useful oxidant. Its ready availability in a state of high purity has made it an excellent *primary standard* for oxidimetric titrations. The reduction potential of the $Cr_2O_7^{2-}/Cr^{3+}$ couple is + 1.33 volts. It can therefore readily oxidise ferrous to ferric and can liberate iodine from iodide ion. Hexavalent chromium is reduced during these reactions to trivalent chromium :

$$K_2Cr_2O_7+6FeSO_4+7H_2SO_4 \rightarrow Cr_2(SO_4)_3+3Fe_2(SO_4)_3+K_2SO_4+7H_2O$$

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 3I_2 + 7H_2O$$

Since there are two hexavalent chromiums per $K_2Cr_2O_7$ it can be easily appreciated that the equivalent weight of the dichromate will be one-sixth the molecular weight (Chapter 29).

On heating, the potassium salt and the ammonium salt decompose in different manners :

$$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$$

Potassium Chromate : This is obtained on concentrating a solution containing one mole $K_2Cr_2O_7$ and one mole of K_2CO_3 (or two moles of KOH). It forms yellow crystals. Reduction potential of the couple CrO_4^{2-}/Cr^{3+} being negative (– 0.13 volts) chromate ion has no oxidising property . K_2CrO_4 and K_2SO_4 are tetrahedral and isomorphous with each other.

Chromyl Chloride : This compound, CrO_2Cl_2, is obtained as a dark red liquid on reacting CrO_3 with HCl or by slight heating of a mixture of an ionic chloride (NaCl) and $K_2Cr_2O_7$ with concentrated H_2SO_4 ;

$$CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O$$

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + 3K_2SO_4 + 3H_2O$$

This is a typical reaction shown by ionic chlorides only. The reaction is not applicable to covalent chloride like $HgCl_2$. It is readily decomposed by water :

$$CrO_2Cl_2 + 2H_2O \rightarrow H_2CrO_4 + 2HCl$$

It is interesting to note that it is not possible to get chromyl bromide or chromyl iodide because the HBr/HI produced in the reaction is easily oxidised to bromine or iodine.

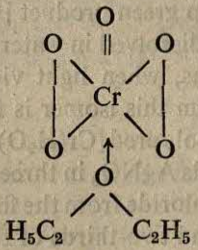
Chrome Red : This is a basic lead chromate, $PbCrO_4.PbO$, obtained by the addition of alkali to a solution of lead nitrate and potassium chromate :

$$Pb(NO_3)_2 + K_2CrO_4 \xrightarrow{\text{dilute NaOH}} \underset{\text{(red)}}{PbCrO_4.PbO}$$

It is used as yellow pigment.

Chrome Yellow : On the addition of potassium chromate to a solution of lead nitrate insoluble lead chromate, $PbCrO_4$, separates as a yellow product. This is known as chrome yellow and is used as a pigment.

Peroxychromate : A blue colour develops on the addition of H_2O_2 to a solution of a chromate or a dichromate in the presence of H_2SO_4. It is highly soluble in ether and can be extracted into the ether layer from aqueous solution. It is believed that in ether the peroxy compound, CrO_5, forms the addition compound $(C_2H_5)_2O \rightarrow CrO_5$. The structure is likely to be as shown below :



This blue coloured compound is made use of in qualitative detection of chromium.

23.3.2. Trivalent Chromium : In Fig. 23.1 synthetic reactions of several chromium (II) compounds are indicated. We discuss below only a few compounds in some details:

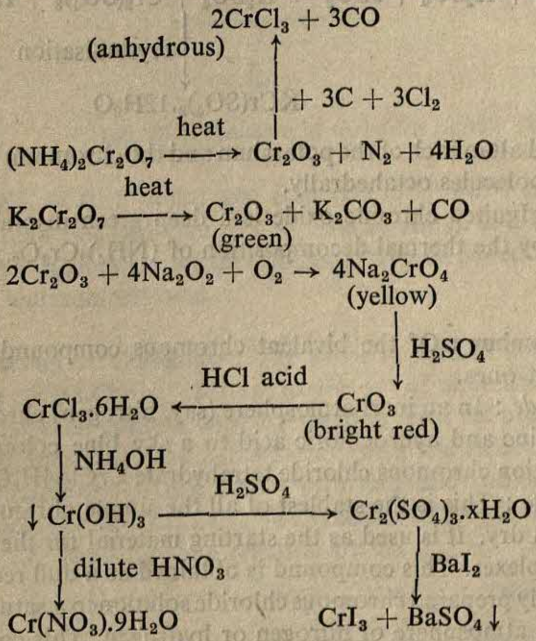


Fig. 23.1. Synthetic routes to some chromium (III) compounds

Chromic Chloride : Anhydrous chromic chloride may be prepared by two methods : (1) by heating green Cr_2O_3 with carbon and chlorine and (2) by direct chlorination of chromium metal. The anhydrous chloride is violet in colour and is insoluble in water and alcohol. This is used as a starting material for the syntheses of many chromium (III) compounds.

Hydrated chromic chloride is prepared by the reduction of CrO_3 by HCl acid. It has six water molecules. However the structure of the compound depends on the mode of synthesis. Three isomeric forms of $CrCl_3.6H_2O$ are known. In the presence of a small amount of $CrCl_2$ the anhydrous $CrCl_3$ readily dissolves in water. From this solution a deep green product $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ can be crystallised. This green product is dissolved in water of its own weight and heated under reflux treated with HCl gas, when light violet coloured $[Cr(H_2O)_6]Cl_3$ crystallises. The mother liquor from this isomer is further treated with HCl gas and finally with ether. Light green coloured $[Cr(H_2O)_5Cl]Cl_2.H_2O$ now crystallises. These three isomers respond towards $AgNO_3$ in three different ways. Silver nitrate precipitates one-third of the total chloride from the first isomer while in the second and the third the entire chloride and two-thirds of the chloride are precipitated. These three compounds have been cited as examples of hydrate isomerism (Chapter 6).

Potassium Chromium Sulphate: This is the commonest alum of chromium. Potassium dichromate is reduced in the presence of sulphuric acid by SO_2 or alcohol :

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

$$\Big\downarrow \text{crystallisation}$$

$$KCr(SO_4)_2.12H_2O$$

In this violet coloured alum each of the potassium and the chromium ion is coordinated by six water molecules octahedrally.

Chrome Green : Ignited chromic oxide is a deep green insoluble material. It may be obtained by the thermal decomposition of $(NH_4)_2Cr_2O_7$. It is used as a green pigment.

23.3.3. Bivalent Chromium : Of the bivalent chromous compounds we discuss only three important ones.

Chromous Chloride : In an inert atmosphere (say, nitrogen) chromic chloride may be reduced by zinc and hydrochloric acid to a sky blue coloured solution. On careful crystallisation chromous chloride tetrahydrate $CrCl_2.4H_2O$ is obtained.

Chromous Acetate : This is the stablest of all the simple chromous compounds particularly when dry. It is used as the starting material for the syntheses of other chromous complexes. This compound is obtained as a dull red product on the addition of a freshly prepared chromous chloride solution to a saturated sodium acetate solution in an atmosphere of nitrogen or hydrogen. This compound is a dimer as shown in Fig. 23.2. The oxygen atoms of the four acetate ions act as bridges between the two chromium (II). There is one H_2O per chromium (II) and furthermore there is a chromium-chromium bond in the dimer. The Cr-Cr distance is 2.46A while $Cr-OH_2$ and $Cr-O$ (acetate) bond lengths are 2.20A and 1.97A respectively.

Chromous Sulphate : This may be prepared by the reaction of chromium metal with zinc and hydrochloric acid or by the reaction of chromous acetate with hydrochloric acid. The compound may be crystallised in an inert atmosphere as a pentahydrate or a heptahydrate depending on the reaction conditions.

The heptahydrate is a real vitriol : $CrSO_4.7H_2O$. It is thus isomorphous with other true vitriols like $FeSO_4.7H_2O$, $ZnSO_4.7H_2O$.

Reducing ability of chromous ion : The chromous ion is fine reducing agent. The reduction potential of the Cr^{3+}/Cr^{2+} couple is -0.41 volts. It is therefore a better reducing agent than vanadium (II) (V^{3+}/V^{2+}, $E° = -0.26$ volts), tin (II) (Sn^{4+}/Sn^{2+}, $E°, = 0.15$ volts) and iron (II) (Fe^{3+}/Fe^{2+}, $E° = 0.77$ volts) but less effective than zinc (Zn^{2+}/Zn, $E° = -0.76$ volts). It is because of the higher reducing ability of metallic zinc that chromic (III) can be reduced to chromium (II) by zinc and hydrochloric acid.

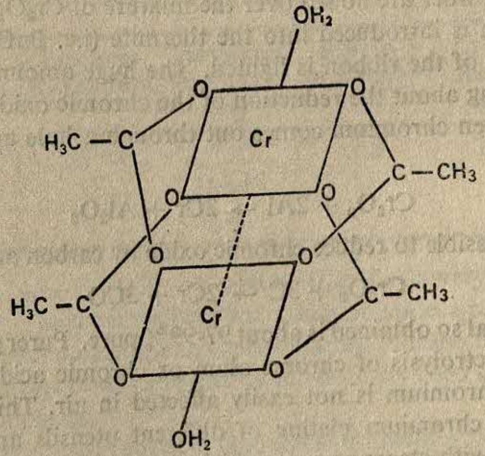


Fig. 23.2. Structure of chromous acetate dimer

23.3.4. Extraction of Chromium : The most important source of chromium is chromite ore : $FeO.Cr_2O_3$. This ore carries lot of undesirable material. The ore is crushed and then concentrated by treating with running water in a shaking table. Lighter impurities are carried alongwith the stream of water.

The chromite ore is then mixed with lime and sodium carbonate and the mixture roasted in a stream of air. The presence of lime helps to keep the mixture pervious to air. The following reaction occurs :

$$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

The mixture is stirred with water, acidified with H_2SO_4 and then treated with KCl. Less soluble $K_2Cr_2O_7$ crystallises :

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

The above potassium salt is mixed with NH_4Cl and the mixture heated when the ammonium dichromate decomposes to give pure Cr_2O_3 :

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$$

Washing with water removes the KCl formed during double decomposition between potassium dichromate and ammonium chloride.

Now Goldschmidt thermit process is applied in reducing the green Cr_2O_3 to metallic chromium (Chapter 17). The chromic oxide is mixed with aluminium powder and the mixture is then taken in a heat resistant crucible. Barium peroxide and magnesium powder are added over the mixture of Cr_2O_3 and Al powder. A magnesium ribbon is introduced into the thermite (i.e. BaO_2 plus Mg powder) and the other end of the ribbon is lighted. The huge amount of heat generated is sufficient to bring about the reduction of the chromic oxide by the aluminium powder. The molten chromium comes out through a hole at the bottom of the crucible :

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$

It has also been possible to reduce chromic oxide by carbon around 1400°C :

$$Cr_2O_3 + 3C \rightarrow 2Cr + 3CO$$

The chromium metal so obtained is about 97-99% pure. Purer grade of chromium is obtained via electrolysis of chrome alum or chromic acid.

Properties : Chromium is not easily affected in air. This is the reason of popularity behind chromium plating of different utensils and related articles. The metal reacts with steam at a very high temperature (about 2000°C) to give the oxide. On heating it also reacts with oxygen :

$$4Cr + 3O_2 \rightarrow 2Cr_2O_3 \ ; \ 2Cr + 3H_2O \rightarrow Cr_2O_3 + 3H_2$$

The metal reacts with hydrochloric acid to give chromous acid and hydrogen. The blue colour of the chromous salt slowly changes to green due to oxidation to chromic chloride :

$$Cr + 2HCl \rightarrow CrCl_2 + H_2$$
$$4CrCl_2 + 4HCl + O_2 \rightarrow 4CrCl_3 + 2H_2O$$

Uses of chromium : Chromium is of enormous importance in alloy steels. Nichrome steel contains 60% nickel, 14% chromium and 15% iron. Nichrome wire is used in the construction of electric furnaces. Stainless steel consists of 64% Fe, 18% Cr and 8% Ni. This alloy steel is corrosion resistant and hence finds use in a variety of cases. Chromium salts such as chrome alum or chromic acid is used as an electrolyte in chromium plating baths. The material to be chromium plated is cleaned and then made the cathode of the electrolytic cell. The fine deposit of metallic chromium on the cathode article not only gives a fine pleasing glistening look but also adds to the durability of the material.

MANGANESE

23.4. A RESUME OF THE CHEMISTRY OF MANGANESE

Table 23.2 gives some characteristic physical properties of the element. The electron distribution of the element is $[Ar]3d^5 4s^2$. This shows that the element has incompletely filled 3*d* orbitals. It has a total of seven electrons beyond the stable electronic configuration of the noble gas argon. In the ground state or in ionic states the element will have incompletely filled *d* orbitals. Hence by definition it is a transition metal. The element can show a whole range of oxidation states :

Table 23.2. Some Properties of Manganese

Element	Atomic Number	Electron Distribution	Ionisation Potential (*ev*)	Electro-negativity	Atomic Radius (A)	Ionic(M^{2+}) Radius (A)
Mn	25	$[Ar]3d^5 4s^2$	7.43 15.64 33.69	1.5	1.26	0.80

+ 7, + 6, + 5, + 4, + 3, + 2, +1 and 0. It is thus a very versatile element of the periodic table. The most well known oxidation states are + 3, + 4 and + 2. Commercially manganese compounds are obtained in these three oxidation states. Other oxidation states are less known and have mostly been stabilised and studied in the form of complexes.

As in chromium, here too, acid character or alkaline character of the metal ion changes with changing oxidation state. In accordance with the general rule the highest valent, namely heptavalent, oxide is entirely acidic in nature. On coming to the lower oxides electronegativity of the metal ion falls and basic character tends to appear. Thus bivalent manganese is wholly basic in character. It reacts with acids to give common manganous salts like $MnCl_2$, $MnSO_4$ etc. Trivalent manganese is mainly basic while the other oxidation states are amphoteric.

As the oxidation state goes up oxidising power increases. On the other hand with lower oxidation states oxidising power decreases and reducing power increases. Manganese (III) to manganese (VII) are all oxidants, heptavalent manganese (eg. $KMnO_4$) being by far the most effective. On the contrary manganese (I) and manganese (0) are reducing in character. Bivalent manganese is stable and is neither an effective oxidant nor a reductant.

Depending on the oxidation state as also on the nature of the compound formed there will be varying number of paired or unpaired electrons. Hence various manganese compounds will exhibit a variety of paramagnetism.

23.4.1. Heptavalent Manganese : In this oxidation state there are only two compounds known : Mn_2O_7 and salt of permanganic acid $HMnO_4$.

Manganese Heptoxide : The compound Mn_2O_7 appears as a thick coloured oil on the addition of cooled concentrated H_2SO_4 to powdered $KMnO_4$. This oil may be cooled in liquid air to give green crystals of Mn_2O_7. It decomposes around 0°C to MnO_2 and oxygen. It may be considered as the anhydride of permanganic acid :

$$Mn_2O_7 + H_2O \rightarrow 2HMnO_4$$

Permanganic Acid and its salts : On treating barium permanganate $Ba(MnO_4)_2$ with H_2SO_4 barium sulphate is precipitated and $HMnO_4$ is formed in solution. The acid is quite unstable and attempts to crystallise the acid give MnO_2, O_3 and H_2O.

Industrial scale preparation of potassium permanganate $KMnO_4$ involves two steps :

1. Pyrolusite (mainly MnO_2) is fused with KOH in presence of air. This gives potassium manganate :

$$4KOH + 2MnO_2 + O_2 \rightarrow \underset{\text{(green)}}{2K_2MnO_4} + 2H_2O$$

The green manganate is dissolved out by water and the solution is then further oxidised.

2. Oxidation of manganate may be achieved by several methods : (*a*) oxidation by ozone, (*b*) oxidation by chlorine and (*c*) anodic oxidation.

$$2K_2MnO_4 + H_2O + O_3 \rightarrow 2KMnO_4 + 2KOH + O_2$$
$$2K_2MnO_4 + Cl_2 \rightarrow 2MnO_4 + 2KCl$$

Anodic oxidation of the manganate is carried out in a porous diaphragmed cell. Outside the anode is taken an alkali solution to serve as the catholyte. Potassium permanganate crystallises in the anode chamber :

at the anode : $MnO_4^{2-} \rightarrow MnO_4^- + e$
at the cathode : $2H^+ + 2e \rightarrow H_2$

Properties : It is one of the finest oxidising agents known. Because of some slight uncertainty in its purity and some slight decomposition on storing has made it unsuitable to be used as a primary standard. It is however used as a secondary standard. Its solution is usually standardised against a standard reductant like oxalic acid or sodium oxalate (Chapter 29). Aqueous solution of $KMnO_4$ is light sensitive and hence it is stored in a brown bottle. Oxidising power of permanganate is pH dependent :

in acid medium : $MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$ ($E°=1.51$ volts)
in alkali medium : $MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2 + 4OH^-$ ($E°=1.23$ volts)

Some examples of reactions of $KMnO_4$ in acid and alkali media are given below :

in acid medium :

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$
$$2KMnO_4 + 16HCl \rightarrow 2MnCl_2 + 2KCl + 5Cl_2 + 8H_2O$$
$$2KMnO_4 + 10KI + 8H_2SO_4 \rightarrow 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$$
$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$
$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

in alkaline solution :

$$2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$$

$$2KMnO_4 + 3HCOOK \rightarrow KHCO_3 + K_2CO_3 + 2MnO_2 + H_2O$$

Note that in acid medium manganese (VII) is being reduced to manganese (II) while in alkaline medium reduction goes to the extent of manganese (IV). Thus in alkaline medium equivalent weight of potassium permanganate is one-third the molecular weight while in acid medium it is one-fifth. In acid medium there occurs a five-electron reduction process whereas in alkaline medium a three-electron process takes place. Potassium permanganate is very intensely coloured and hence it can serve as its own indicator in redox titrations. This is one advantage over potassium dichromate.

Problem 1. 18 ml. of 0.1 M $KMnO_4$ solution is required in the titration of 20 ml of an acidified ferrous solution. Find the strength of the ferrous solution in molarity.

From the equations of permanganate reactions in acid medium we know 1 mole permanganate can oxidise 5 moles of ferrous to ferric. Let us now calculate how many moles of permanganate are there in 18 ml of 0.1 M $KMnO_4$.

$$18 \text{ ml of } 0.1 \ M \ KMnO_4 \equiv \frac{18 \times 0.1}{1000} = 0.0018 \text{ mole}$$

$0.0018 \text{ mole } KMnO_4 = 5 \times 0.0018 \text{ mole} = 0.009 \text{ mole ferrous}$

Thus 20 ml ferrous solution really contains 0.009 moles.

$$\text{Strength of the ferrous solution} = \frac{0.009 \times 1000}{20} = 0.45 \ M$$

The strength can be calculated in an alternative way also. Since 1 mole of $KMnO_4$ is equivalent to 5 moles of $KMnO_4$ we can write :

18 ml of 0.1 M $KMnO_4$ = 18 ml of 0.1 × 5 M ferrous

This strength is contained in the 20 ml of the ferrous solution.

$$\text{The strength of the ferrous solution} = \frac{18 \times 0.1 \times 5 \times 1000}{20} = 0.45 \ M$$

Problem 2. 0.6428 gram of iron ore was dissolved in acid, reduced with stannous chloride and finally titrated with 0.1052 N $KMnO_4$ solution. The volume of permanganate required was 36.3 ml. Calculate the percentage of iron in the ore.

$1 \text{ ml. } N \ Fe^{2+} \equiv 1 \text{ ml. } N \ KMnO_4$

$1000 \text{ ml. } N \ Fe^{2+} \equiv 55.85 \text{ gram iron} \ ; \ 1 \text{ ml. } N \ Fe^{2+} \equiv 0.05585 \text{ gm iron}$

Total iron in 0.6428 gram iron ore = 36.3 × 0.1052 × 0.05585 gram

$$\text{Therefore percentage iron} = \frac{36.3 \times 0.1052 \times 0.05585 \times 100}{0.6428} = 33.18\%$$

Problem 3. The calcium content of a solution containing 1.65 gram of a calcium salt was completely precipitated as CaC_2O_4. The oxalate was dissolved in acid and the liberated oxalic acid was titrated with 0.11 M $KMnO_4$ solution. The titre value was 18.0 ml. Calculate the percentage of calcium in the salt,

$0.11\ M\ KMnO_4 \equiv 0.55\ N\ KMnO_4$

18 ml. of $0.55\ N\ KMnO_4 \equiv$ 18 ml. of $0.55\ N\ C_2O_4{}^{2-}$

1000 ml. $1\ N\ C_2O_4{}^{2-} \equiv$ 44 gram $C_2O_4{}^{2-} \equiv$ 20 gram Ca^{2+}

$$\text{Percentage of calcium} = \frac{18 \times 0.55 \times 20 \times 100}{1000 \times 1.65} = 12\%.$$

23.4.2. Hexavalent Manganese : This oxidation state of manganese is known only in the salts of manganic acid H_2MnO_4. Manganate salts can be prepared by two different methods :

1. Potassium manganate is obtained by heating a mixture of MnO_2 and KOH in a stream of air :

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{heat}} 2K_2MnO_4 + 2H_2O$$

2. Alternatively a mixture of MnO_2 and KNO_3 may be heated :

$$MnO_2 + 2KNO_3 \xrightarrow{\text{heat}} K_2MnO_4 + 2NO_2$$

Potassium manganate is soluble in water. The solid manganate may be crystallised from this solution. This is stable in alkaline solution but undergoes *valence disproportionation* into a compound of lower valence and one of higher valence in acid or neutral media :

$$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + 4KOH + MnO_2$$

$$3K_2MnO_4 + 2H_2SO_4 \rightarrow 2KMnO_4 + MnO_2 + 2K_2SO_4 + 2H_2O$$

Manganate salts are oxidants. The manganate ion is isomorphous with chromate and sulphate ions. Hexavalent manganese may be viewed as a $3d^1$ system and hence manganate salts are paramagnetic.

23.4.3. Quadrivalent Manganese : The major natural ore of manganese is pyrolusite which is basically the oxide of quadrivalent manganese, MnO_2. All other compounds of quadrivalent manganese are complex compounds. This oxide is amphoteric in nature. As a basic oxide it dissolves in acids to give compounds of the type M_2MnX_6 or MnX_4. MnO_2 also reacts with bases to form manganites M_2MnO_3.

In acid medium MnO_2 functions as an oxidant :

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

$$MnO_2 + H_2SO_4 + H_2O_2 \rightarrow MnSO_4 + 2H_2O + O_2$$

$$MnO_2 + H_2SO_4 + H_2C_2O_4 \rightarrow MnSO_4 + 2CO_2 + 2H_2O$$

$$MnO_2 + 2H_2SO_4 + 2FeSO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + 2H_2O$$

Careful treatment of $MnSO_4$ by $KMnO_4$ in presence of H_2SO_4 gives blackish crystals of $Mn(SO_4)_2$. This is however hydrolysed to MnO_2. Manganous nitrate decomposes on heating to MnO_2 and NO_2 :

$$Mn(NO_3)_2 \rightarrow MnO_2 + 2NO_2$$

MnO_2 is insoluble in water and is thus stable. The hydroxide obtained by the action of alkali on manganese (II) or manganese (III) is oxidised in air to the dioxide MnO_2.

We have already mentioned that manganese occurs in nature as the dioxide, pyrolusite, (MnO_2). The quality of pyrolusite is determined by the active oxygen it contains i.e. by its oxidising ability. This is evaluated by reacting a known weight of the pyrolusite with an excess of standard oxalic acid or arsenious acid. After the entire quantity of the pyrolusitehas reacted the excess oxalic acid or the arsenious acid is back titrated with a standard solution of $KMnO_4$. From the knowledge of the amount of the reducing agent that reacted with the pyrolusite it is possible to determine the percentage of the active oxygen and hence the MnO_2 in the ore.

Problem 1. 0.09 gram of pyrolusite was boiled with 25 ml. of sodium oxalate ($N/10$) in the presence of 25 ml. of 2 N H_2SO_4. The excess oxalic acid was then back titrated with ($N/10$) $KMnO_4$. This titration required 15 ml of the permanganate. Calculate the percentage of MnO_2 and the active oxygen in the ore.

15 ml 0.1 N $KMnO_4$ = 15 ml. 0.1 N $Na_2C_2O_4$

Therefore 0.09 gram pyrolusite = $25 - 15 \simeq 10$ ml. 0.1 N $Na_2C_2O_4$

1000 ml of N $Na_2C_2O_4$ = $\frac{1}{2}(Na_2C_2O_4)$ = $\frac{1}{2}(MnO_2)$ = 43.47 gram MnO_2

(Note the reaction : $H_2C_2O_4 + H_2SO_4 + MnO_2 \rightarrow MnSO_4 + 2CO_2 + 2H_2O$)

1000 ml. of 0.1 N $Na_2C_2O_4$ = 4.347 gram of MnO_2

$$\text{Percentage of } MnO_2 \text{ in the ore} = \frac{4.347 \times 10 \times 100}{1000 \times 0.09} = 48.3\%\ MnO_2$$

Calculation of active oxygen : $MnO_2(86.94) \rightarrow MnO + O(16)$

$$\text{Percentage of active oxygen} = \frac{16 \times 48.3}{86.94} = 8\%$$

23.4.4. Trivalent Manganese : In this oxidation state the element is entirely basic. A few compounds of simple formula are known. The action of fluorine on MnI_2 produces red crystals of MnF_3. Deep brown coloured manganic acetate can be obtained by oxidising manganous acetate in hot glacial acetic acid medium with $KMnO_4$ or chlorine. Manganese (III) produces alums. Anodic oxidation of $MnSO_4$ in a diaphragmed cell in presence of moderately concentrated H_2SO_4 gives rose coloured $Mn_2(SO_4)_3$ in solution. This solution is treated with a solution of tetramethylammonium sulphate in H_2SO_4 and allowed to crystallise at 5°C. Crystals of rose coloured alum $[N(CH_3)_4]\ Mn(SO_4)_2.12H_2O$ are thus obtained. Manganese (III) salts liberate one equivalent of iodine from acidified potassium iodide :

$$2Mn^{3+} + 2I^- \rightarrow 2Mn^{2+} + I_2$$

23.4.5. Bivalent Manganese : This oxidation state of manganese is the most well known. A wide variety of compounds is known. Bivalent manganese is entirely basic. Its salts are very pale pink coloured. Compounds of bivalent manganese are commonly prepared by reacting MnO_2 with suitable acids :

$$\underset{\text{(pyrolusite)}}{2MnO_2} + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O + O_2$$

Since pyrolusite contains some iron the manganese compounds also contain $FeSO_4/Fe_2(SO_4)_3$. Pure $MnSO_4$ may be obtained by fractional crystallisation. Alternatively the reaction solution is treated with a small amount of NH_4OH when $Fe(OH)_3$ is precipitated. The filtered solution will give crystals of the vitriol $MnSO_4.7H_2O$. Reaction of MnO_2 with HCl will furnish $MnCl_2.4H_2O$. Alternatively MnO_2 may be heated with NH_4Cl :

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$

$$3MnO_2 + 6NH_4Cl \rightarrow 3MnCl_2 + 4NH_3 + N_2 + 6H_2O$$

Manganous nitrate $Mn(NO_3)_2.6H_2O$ is usually prepared by reacting the carbonate with nitric acid. On heating the compound decomposes :

$$Mn(NO_3)_2 \xrightarrow{\text{heat}} MnO_2 + 2NO_2$$

Extraction of Manganese : The major ore is pyrolusite MnO_2. It is contaminated with Fe_2O_3, SiO_2 and Al_2O_3. This ore is found in our country in some areas of Karnataka, Bihar, Orissa, Nagpur. This valuable ore is mostly exported to other countries. Besides pyrolusite there are a few less known ores : braunite, Mn_2O_3 ; manganite, $Mn_2O_3.H_2O$, rhodochrosite $MnCO_3$.

Extraction of manganese from pyrolusite may be achieved by two methods : (*a*) Goldschmidt thermite process and (*b*) electrolytic process.

1. *Goldschmidt thermite process* : Pyrolusite ore is finely powdered and then the magnetic ferric oxide impurity is removed with the help of a magnetic field. The concentrated ore is next mixed with aluminium powder and taken in a heat resistant crucible (Chapter 17. Fig. 17.4). The thermite mixture (BaO_2 plus magnesium powder) is added. One end of a magnesium fuse is introduced into the thermite and the other end is lighted. The thermite reacts and the liberated heat brings about the reduction of the pyrolusite to manganese metal. The liquid metal passes out through a hole at the bottom of the crucible :

$$3MnO_2 + 4Al \rightarrow 3Mn + 2Al_2O_3$$

2. *Electrolytic process* : The pyrolusite is first treated with acids when salts like $MnCl_2$, $MnSO_4$ are produced. Usually the manganous sulphate salt solution is used as the electrolyte. A diaphragmed cell is used. The anode compartment contains a solution of $MnSO_4$, $(NH_4)_2SO_4$ and H_2SO_4 adjusted to pH 1. The cathode solution has aqueous $MnSO_4$ at pH 7.5. Powdered manganese collects at the cathode.

Properties : Manganese reacts with acids or even water to liberate hydrogen :

$$Mn + H_2SO_4 \rightarrow MnSO_4 + H_2\uparrow$$

$$Mn + 2H_2O \rightarrow Mn(OH)_2 + H_2\uparrow$$

The following reactions also occur, sometimes with the aid of heat :

$$Mn + Cl_2 \rightarrow MnCl_2 \quad ; \quad 3Mn + N_2 \rightarrow Mn_3N_2$$

$$Mn + S \rightarrow MnS$$

Uses : Magnanese has enormous demand in industry. It is a constituent of several important alloy steels. Ferromanganese contains 70-80% Mn and 20-30% iron. Spigeleisen is composed of 15-20% manganese and the rest iron. Steel containing 8-10% manganese is very hard and resistant to corrosion. Compositions of two other manganese bearing alloys are given below :

manganese bronze : Cu, 55-65% ; Mn 16-17% ; Zn, 20-30%
manganin : Cu, 84% ; Mn, 12% ; Ni, 4%

Manganese alloy steels are used in the construction of rails and fast moving instruments. Manganin is used in electric equipments.

IRON, COBALT AND NICKEL

23.5. A RESUME OF THE CHEMISTRY OF IRON, COBALT AND NICKEL

These three elements occupy an important position among the members of the first transition series. Some of their compounds are too well known as catalysts in several industrial processes. These elements have gone a long way to enrich the entire arena of coordination chemistry besides giving interesting compounds in abnormal oxidation states. Their chemistries are so very close that Mendeleev allotted a single place for all three of them in his periodic table. He could not arrange one group for each of these three elements as in that case the logical chemical arrangement of the later elements in the periodic table would have been disturbed. In the long form periodic table also these three elements have been included in the same group eight. In view of their position we first discuss their chemistries on a comparative basis and thereafter we shall take up the discussion on individual basis.

Table 23.3 records some of the important physical characteristics of these elements. Their electron distributions reveal that in the ground state or in some of their oxidation states thrse 3*d* orbitals will remain incompletely filled. Hence by definition they come under transition elements. The first ionisation potentials for all three of them are the same. Atomic radii are practically the same. Bivalent ionic radii decrease slightly with increasing atomic number in accordance with lanthanide contraction (Chapter 4). Melting and boiling points are

Table 23.3. Some Properties of Iron, Cobalt and Nickel

Element	Atomic Number	Electron Distribution	Ionisation Potential (*ev*)	Atomic Radius (A)	Ionic Radius (M^2 ; A)	M.P (°C)	B.P (°C)
Fe	26	$[Ar]3d^64s^2$	7.9	1.26	0.76	1535	2735
Co	27	$[Ar]3d^74s^2$	7.86	1.26	0.74	1480	3550
Ni	28	$[Ar]3d^84s^2$	7.63	1.25	0.69	1455	2732

quite high. Their reduction potentials become less negative with increasing atomic number: $E°$ for M^{2+}/M couples: iron, − 0.44; cobalt, − 0.277; nickel, − 0.25 volts. This indicates that with increasing atomic number the elements tend to be less electropositive in nature.

Common characteristics of transition elements are observed in this series quite well. For example all three exhibit variable valence :

Elements	*Oxidation Numbers*					
Iron	+ 6	+ 4	$+\underline{3}$	$+\underline{2}$	+ 1	0
Cobalt	. . .	. . . .	$+\underline{3}$	$+\underline{2}$	+ 1	0
Nickel	. . .	+ 4	+ 3	$+\underline{2}$	+ 1	0

The underlined oxidation states are quite stable. Many simple and complex compounds are known in these states. For the other states stabilisation has been achieved through complex formation. The following informations also demonstrate that their compounds are generally coloured :

Iron	VI K_2FeO_4 (deep purple)	III $FeCl_3.6H_2O$ (yellow)	II $FeSO_4.7H_2O$ (light green)
Nickel	IV $K[Ni(IO_6)]$ (dark purple)	II $NiSO_4.7H_2O$ (green)	
Cobalt	III $[Co(NH_3)_6]Cl_3$ (orange)	II $CoCl_2.6H_2O$ (light rose)	

Depending on the valence and the nature of the compounds these elements show paramagnetism of different magnitude. With all spins paired, however, there will be diamagnetism as in the cases of almost all the trivalent cobalt complexes (spin paired $3d^6$) system.

Comparison of some chemical properties : In general acid character of an oxide increases with increasing oxidation number and hence with increasing electronegativity. This is readily shown by the fact the hypothetical hexavalent iron oxide, FeO_3, must be acidic as this state is stabilised only in strongly alkaline medium : $FeO_3 + K_2O \rightarrow K_2FeO_4$. Bivalent iron, because of its lower valence, is entirely basic as its hydroxide readily reacts with acid to produce different salts : $Fe(OH)_2 + 2HX \rightarrow FeX_2 + 2H_2O$. Trivalent iron is slightly amphoteric. While bivalent nickel is purely basic quadrivalent nickel compounds have mostly been stabilised in presence of bases. Bivalent cobalt is also basic as it produces all salts in acid medium.

In the bivalent states all these three elements give pure vitriols $FeSO_4.7H_2O$; $CoSO_4.7H_2O$ and $NiSO_4.7H_2O$. The bivalent sulphates combine with monovalent sulphates to form double sulphates of the schonite series :

$(NH_4)_2SO_4.FeSO_4.6H_2O$ (commonly known as Mohr's salt)
$(NH_4)_2SO_4.CoSO_4.6H_2O$
$(NH_4)_2SO_4.NiSO_4.6H_2O$

As can be guessed these double sulphates are isomorphous with each other. Alums of trivalent iron and trivalent cobalt are known. Those of trivalent nickel are not yet known :

$$KFe(SO_4)_2.12H_2O \ ; \ (NH_4)_2Fe(SO_4)_2.12H_2O \ ; \ KCo(SO_4)_2.12H_2O$$

Nitrates of the bivalent elements all crystallise with six molecules of water :

$$Fe(NO_3)_2.6H_2O \ ; \ Co(NO_3)_2.6H_2O \ ; \ Ni(NO_3)_2.6H_2O$$

The carbonyls of all these three elements, apparantly in the zero oxidation states, are very well known. The finely divided elements react under varying conditions of temperature and pressure to give the carbonyls. In fact there are a large number of their carbonyls. We give the simplest of these only :

$$Fe(CO)_5 \ ; \ Co_2(CO)_8 \ ; \ Ni(CO)_4.$$

Nickel tetracarbonyl is famous because of the fact that very pure nickel is prepared by the thermal decomposition of this carbonyl.

IRON

23.6.1. Hexavalent Iron : This oxidation state of iron is representated by only one class of compounds, namely the salts of the hypothetical ferric acid H_2FeO_4. It is usually prepared by the chlorine oxidation of an alkaline suspension of ferric hydroxide. Sodium hypochlorite is initially produced, which brings about the oxidation :

$$2Fe(OH)_3 + 3NaOCl + 4NaOH \rightarrow 2Na_2FeO_4 + 3NaCl + 5H_2O$$

After filtering off any unreacted ferric hydroxide through a sintered glass funnel a deep purple solution of sodium ferrate Na_2FeO_4 is obtained. On dropping this solution over solid KOH the potassium ferrate K_2FeO_4 is obtained in the crystalline form. K_2FeO_4 is a very powerful oxidising agent :

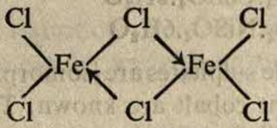
$$2NH_4OH + 2K_2FeO_4 \rightarrow 2Fe(OH)_3 + N_2 + 4KOH$$
$$Cr(OH)_3 + K_2FeO_4 \rightarrow K_2CrO_4 + Fe(OH)_3$$

The ferrate ion is tetrahedral and is obviously isomorphous with similar ions like sulphate, selenate and chromate. The potassium salt is paramangnetic to the extent of two unpaired spins, typical of a $3d^2$ system.

23.6.2. Trivalent Iron : *Ferric Halides* : Anhydrous $FeCl_3$ is prepared by the reaction of dry chlorine with iron filings in a heated tube. At a temperature of about 300°C anhydrous $FeCl_3$ sublimes and is collected in a suitable container provided with a suitable guard tube packed with a dehydrating agent :

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

The compound is highly hygroscopic. In the presence of HCl crystals of the hydrated salt, $FeCl_3.6H_2O$, are obtained. In the gaseous state and in some organic solvents like ether the anhydrous compound exists as a dimer :



On heating in vacuum the compound decomposes into $FeCl_2$ and chlorine.

Ferric bromide and ferric fluoride are known but not the iodide. The non-existence of the iodide salt is easily understandable because the iodide ion is oxidised by the ferric ion :

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

The properties of the fluoride and the bromide are parallel to those of the chloride.

Ferric Sulphate : Reaction of sulphuric acid with iron filings gives ferrous sulphate. This solution is then oxidised by nitric acid to get crystals of ferric sulphate :

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$
$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

Ferric Alum : Equimolar proportions of ferric sulphate and potassium (or ammonium) sulphate are mixed, concentrated and allowed to crystallise :

$$KFe(SO_4)_2.12H_2O \;;\; NH_4Fe(SO_4)_2.12H_2O.$$

Ferric Nitrate : This is obtained by reacting iron with concentrated nitric acid. On concentration very light violet crystals of $Fe(NO_3)_3 : 9H_2O$ are obtained. This is very hygroscopic.

Ferric Hydroxide : This is precipitated as a brown insoluble matter on the addition of ammonia or alkali to a solution of a ferric salt. It is written as $Fe(OH)_3$ or $Fe_2O_3.xH_2O$. It has some weak amphoteric properties. It easily dissolves in acid to give ferric salts indicating that it is a basic oxide. It is also soluble to some extent in hot concentrated alkali. It is possible to crystallise sodium/potassium ferrite from this solution :

$$FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl$$
$$Fe(OH)_3 + NaOH \rightarrow NaFeO_2 + 2H_2O$$

On heating ferric hydroxide we get Fe_2O_3, which is the weighing form of a gravimetric procedure of determination of iron (Chapter 29). Fe_2O_3 is used in many cases as a catalyst (e.g. in the reaction of water gas and steam ; Chapter 18).

23.6.3. Bivalent Iron : *Ferrous Sulphate* : This is obtained by the reaction of iron or iron sulphide with sulphuric acid. It crystallises as a vitriol : $FeSO_4.7H_2O$.

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2 \; ; \; FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$$

On heating ferrous sulphate heptahydrate first loses the six molecules of water to form the monohydrate $FeSO_4.H_2O$. On careful heating the anhydrous $FeSO_4$ is formed. On further heating the compound decomposes finally to ferric oxide :

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

Volumetric estimation of ferric iron is often done via reduction to the ferrous state and there after the ferrous is titrated by a standard oxidant like dichromate or permanganate. Some of the reduction reactions of ferrous iron are indicated below :

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

$$2FeSO_4 + H_2O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2H_2O$$

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

Mohr's Salt : This is a schonite series double sulphate between ferrous iron and ammonium ion. A saturated solution of ferrous sulphate and ammonium sulphate in equimolar proportion at about 40°C is allowed to crystallise to get the Mohr's salt : $FeSO.(NH_4)_2SO_4.6H_2O$. In volumetric analyses it is used as a standard. It is also used as a standard in magnetic susceptibility measurments.

Ferrous Halides : All the four halides are known. Ferric fluoride may be reduced by hydrogen to FeF_2.$FeCl_2$ may be obtained by a similar method. Anhydrous $FeBr_2$ and FeI_2 are prepared by the action of the corresponding halogens on excess iron.

The hydrated halides may be prepared by the action of aqueous halogen hydracids on iron : $FeF_2.8H_2O$; $FeCl_2.6H_2O$; $FeBr_2.6H_2O$ and $FeI_2.4H_2O$. The fluoride is colourless while the other three are light green.

Ferrous Hydroxide : The pure white hydroxide is precipitated in a nitrogen or hydrogen atmosphere on the addition of alkali to a ferrous solution :

$$FeSO_4 + 2NaOH \rightarrow Fe(OH)_2 + Na_2SO_4$$

In presence of air it is partially oxidised to a green product, which turns brown to $Fe(OH)_3$ on oxidation.

Ferrous Sulphide : A vigorous reaction occurs on heating a mixture of powdered sulphur and iron to give FeS : $Fe + S \rightarrow FeS$. This liberates H_2S on reaction with acids.

Potassium Ferrocyanide and Ferricyanide : Preparation of potassium ferrocyanide, $K_4Fe(CN)_6$, can be easily achieved in the laboratory. On the addition of KCN to aqueous ferrous sulphate a precipitate of ferrous cyanide, $Fe(CN)_2$, is first formed. This precipitate dissolves out on the addition of excess cyanide to form the ferrocyanide complex. The solution is next concentrated and cooled to get the yellow crystals of potassium ferrocyanide :

$$FeSO_4 + 2KCN \rightarrow Fe(CN)_2 + K_2SO_4$$
$$Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]$$

Industrial scale preparation involves heating together a mixture of animal blood, horns, hide powder etc, iron powder and potassium carbonate. The reaction product is leached with water and filtered. The filtrate is concentrated and cooled to get $K_4[Fe(CN)_6]$.

Potassium ferricyanide, $K_3[Fe(CN)_6]$, is obtained by the oxidation of potassium ferrocyanide with either chlorine or potassium permanganate :

$$2K_4[Fe(CN)_6] + Cl_2 \rightarrow 2K_3[Fe(CN)_6] + 2KCl$$
$$5K_4[Fe(CN)_6] + KMnO_4 + 8HCl \rightarrow 5K_3[Fe(CN)_6] + 6KCl + MnCl_2 + 4H_2O$$

Prussian Blue and Turnbull's Blue : The deep blue precipitate obtained on the addition of *ferricyanide to a ferrous solution* is called Turnbull's blue and is commonly given the formula $KFe^{II}[Fe^{III}(CN)_6]$. On the other hand a deep blue precipitate, called Prussian blue, is also formed on the addition of *ferrocyanide to a ferric solution* and is commonly represented as $KFe^{III}[Fe^{II}(CN)_6]$. It is now believed that both the blue precipitates are in reality the same. Note that each molecule contains the same number of potassium, ferrous, ferric and cyanide ions. Structural studies indicate that the unit cell of both the Turnbull's blue and Prussian blue is composed of the same ions. These precipitates help in the qualitative detection of both ferrous and ferric ions.

Sodium Nitroprusside : This is nitrosyl pentacyano ferriate (II), $Na_2[Fe(CN)_5(NO)]$. The compound may be obtained by two methods. In one method a solution of $Na_4[Fe(CN)_6]$ and sodium nitrite is acidified with HCl and the solution allowed to crystallise :

$$Na_4[Fe(CN)_6] + NaNO_2 \rightleftharpoons Na_4[Fe(CN)_5(NO_2)] + NaCN$$
$$Na_4[Fe(CN)_5(NO_2)] + 2HCl \rightleftharpoons Na_2[Fe(CN)_5(NO)] + 2NaCl + H_2O$$

An alternative procedure involves reacting a concentrated solution of $Na_4[Fe(CN)_6]$ with 1 : 1 HNO_3 and finally neutralising the reaction mixture with sodium carbonate :

$$3H_4[Fe(CN_6)] + HNO_3 \rightarrow 3H_3[Fe(CN)_6] + NO + 2H_2O$$
$$H_3[Fe(CN)_6] + NO \rightarrow H_2[Fe(CN)_5(NO)] + HCN$$

This compound is an important reagent for the detection of sulphide ion. In alkaline solution a sulphide reacts with a dilute solutin of sodium nitroprusside to give a deep violet soution :

$$\underset{\text{(red)}}{Na_2[Fe(CN)_5(NO)]} + Na_2S \rightarrow \underset{\text{(violet)}}{Na_4[Fe(CN)_5(NOS)]}$$

23.6.4. Extraction of Iron : In the modern world the element which is in greatest demand is iron. In the abundance list of all elements this is the fourth. In modern civilisation and scientific pursuits we cannot conceive of doing without it. It is indeed the workhorse of all metals. There are bountiful deposits of iron ore spread over many countries of the world. There are some highly advanced countries like Japan, which do not have any iron deposit of their own but have made up this deficiency by importing the ore from other countries (like ours) and then turning out high quality iron and steel for export.

The two major iron ores are : hematite, Fe_2O_3 and magnetite, Fe_3O_4. The hematite ore is red in appearance while the magnetite is black. In the United States there are huge deposits of iron ore in Minnesota, Michigan, Wisconsin. Labrador in South America, Sweden and the U.S.S.R also have huge deposits. India too has good deposits in Bihar, Orissa, Madhya Pradesh, Andhra Pradesh, Karnataka and West Bengal.

The actual process employed in the recovery of iron from its ores depends on the type of the iron desired. Different types of iron arise out of the varying carbon content. Three important forms are :

1. Pig Iron or Cast Iron ($\sim 4\%$ C)
2. Steel (~ 0.15 to 1.5% C)
3. Wrought Iron ($0.1 - 0.25\%$ C)

Extraction of iron from its major source hematite involves the following three steps :

I. Concentration of the ore II. Converison of the ore to pig iron
III. Refining : Conversion of pig iron to steel

I. CONCENTRATION OF THE ORE : The raw ore obtained direct from the mines contains many undersirable materials. To increase the efficacy of the extraction process the raw ore needs to be processed through several stages in order to increase the percentage of the iron oxide. Concentration is achieved in three steps :

A. Gravity separation : When there is a marked difference in the specific gravity of hematite and the accompanying waste rock, called *gangue*, gravity separation is used. The powdered raw ore is treated on a shaking table with a running stream of water. The ore and the gangue can thus be separated to some extent.

B. Froth Floatation process : The powdered ore is treated with water and some pine oil and the mixture agitated with a stream of air. Such agitation of two immiscible liquids by air leads to the formation of froth which preferentially carries most of the real hematite ore. The froth is separated and the enriched ore collected.

C. Magnetic Separation : Since the iron ores are mangetic in nature while the impurities are not or very less so, magnetic separation pays rich dividend. The powdered ore is allowed to travel over a running belt in a magnetic field.

The magnetic hematite is deposited close to the magnetic field while the non-magnetic gangue collects farther away.

II. Conversion of the ore to pig iron : Conversion of the red hematite ore to the master metal is a process which has taken scientists and engineers many hundred years to bring to perfection. The conversion is carried out in modern *blast furnaces*. A blast furnace is a huge cylinder made of steel. Depending on the amount of the ore to be processed its height may vary from 120 to even 200 feet. The inside of the furnace is lined with very high melting refractory bricks. The diameter of the furnace gradually increases from its base to a point above the nozzoles for pushing in the blast of preheated air. These nozzoles are called *tuyeres*. The diamater then gradually decreases and becomes quite small at the top. At the top the mouth of the furnace is provided with a *cup and cone* arrangement. This arrangement is such that the mouth of the furnace opens under the pressure of the raw materials that are added from time to time. After the raw materials are added the mouth closes on its own due to the upward thurst of the gases produced during the operation of the furnace (Fig. 23.3) and due to the downward movement of the weight attached to the cup and cone arrangement. There is a side exit tube towards the top for the issuing gases. These hot gases (CO, N_2 and CO_2) are first led to dust collector and then to stoves for heating the air that will be forced under pressure through the tuyeres. The temperature of the preheated air is around 600°C. Depending on the size of the blast furnace about 70 to 100 tons of preheated air are fed into the blast furnace each hour. It is possible to prepare 800-3000 tons of pig iron per day using blast furnace of suitable dimension. A blast furnace may continue to work non-stop for about five years. Thereafter operation is stopped and the furnace is overhauled. The raw materials for the operation i.e the blast furnace charge is carried to the mouth of the furnace by skip cars. The raw materials consist of concentrated hematite, limestone and coke. The coke is obtained by the burning of coal in coke oven batteries such that all volatile components

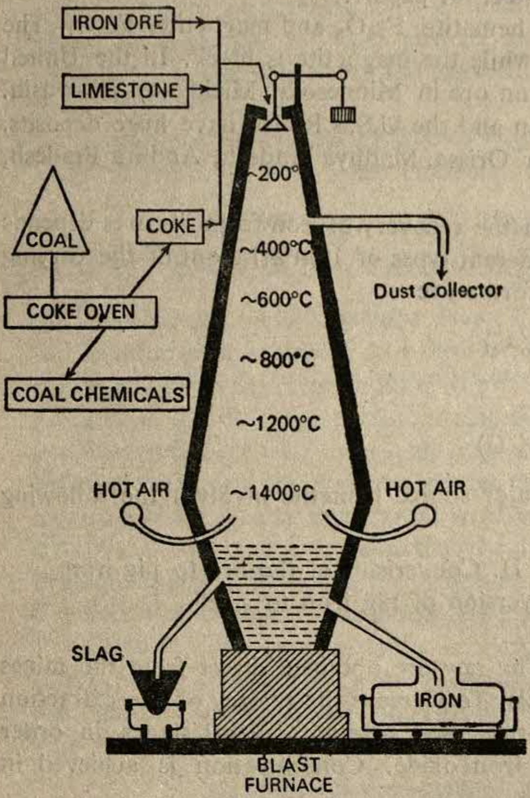


Fig. 23.3. Blast furnace

are removed. The white-hot coke is pushed from coke ovens into suitable carriers and is immediately drenched by water so that it cannot burn out in air. Coke is extremely suited for the purpose. In air it produces CO with liberation of heat. This CO is the major reducing agent in the blast furnace.

Reactions inside the blast furnace : The raw materials for the blast furnace reaction consist of enriched hematite (Fe_2O_3), coke and limestone ($CaCO_3$). Depending on the quality of the iron ore the ratio of hematite, coke and limestone varies. Usually it is 5 : 2 : 1 but may sometimes be 12 : 5 : 3. As the charge descends the blast furnace it meets higher and still higher temperature. The temperature inside an operating blast furnace near the mouth is only ~ 200°C while little above the tuyere it is about ~ 1400°C. Because of the variation in the temperature and because of the preheated air blast series of chemical reactions continue to take place :

$$C + O_2 \rightarrow CO_2 \;;\; CO_2 + C \rightarrow 2CO \;;\; C + \tfrac{1}{2}O_2 \rightarrow CO$$

As the charge slowly descends the blast furnace the following reactions take place :

$$\left.\begin{aligned} 3Fe_2O_3 + CO &\rightarrow 2Fe_2O_3 + CO_2 \\ Fe_3O_4 + CO &\rightarrow 3FeO + CO_2 \\ FeO + CO &\rightarrow Fe + CO_2 \\ Fe_2O_3 + 3CO &\rightarrow 2Fe + 3CO_2 \\ Fe_2O_3 + 3C &\rightarrow 2Fe + 3CO \end{aligned}\right\} \text{These reactions take place within temperature range 300-900°C.}$$

Besides the above basic reactions the impurities in the ore and the limestone also react to form the slag, thus removing the undesirable materials :

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + Al_2O_3 \rightarrow Ca(AlO_2)_2 \;;\; CaO + SiO_2 \rightarrow CaSiO_3$$

If the ore contains some amount of MnO_2 or phosphate these are also decomposed at the strong heat :

$$MnO_2 + 2C \rightarrow Mn + 2CO$$

$$P_4O_{10} + 10C \rightarrow 10CO + P_4$$

At the lower end of the blast furnace the iron and the slag stay in the fused state — fused iron forming the lower layer while the slag forms the upper layer. There are two tap holes for taking out the slag and the iron (Fig. 23.3). Because of the presence of some carbon (~ 4%) impurity the melting point of the iron is lowered from that of the pure iron (1535°C) to about 1200°C. Presence of too much carbon makes the iron brittle and unsuitable for many purposes. In the next step much of this carbon is removed and the pig iron is then transformed into steel.

III. REFINING : CONVERSION OF PIG IRON TO STEEL : Compared to pig iron steel contains much less of carbon. Steel is thus softer and more malleable than pig iron. Conversion of pig iron to steel is a purification process. This purification can be achieved in several ways :

1. *Bessemer Process* : This process was developed by Bessemer in 1856. The purification process consists of oxidising the impurities accompanying pig iron by a blast of air through the molten pig iron taken in an egg-shaped vessel called the Bessemer converter (Fig. 23.4). The outside of the converter is made of good quality steel and the inside is lined with heat-resistant refractory bricks. Depending on the actual impurities in the pig iron the inside of the Bessemer converter is lined with siliceous material (in the absence of phosphorus) or with a mixture of lime and magnesia (in the presence of phosphorus). The converter is so placed over the floor of the steel mill and so fixed with pinions at the sides that it can be tilted, set upright or even inverted at will. The main reactions are conversion of the carbon to carbon monoxide and silicon to silica, wihich then combines with some iron oxide to give the slag. Pig iron is transferred from the blast furnace to the Bessemer converter directly. Air or air mixed up with oxygen is forced through the bottom of the converter. The following reactions take place :

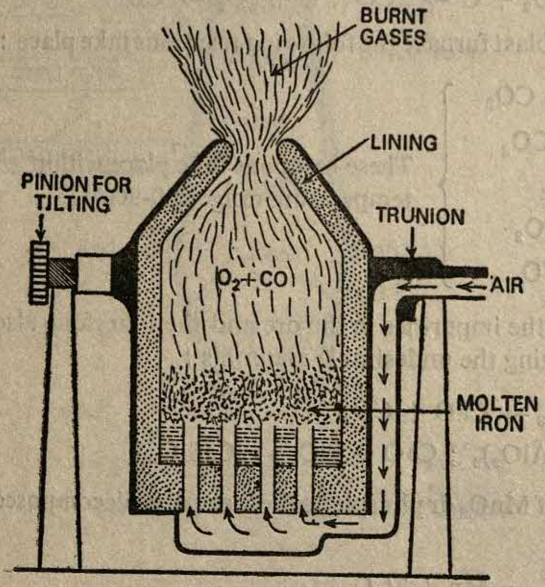


Fig. 23.4. Bessemer converter

$$Si + O_2 \rightarrow SiO_2$$
$$2Mn + O_2 \rightarrow 2MnO$$
$$2Fe + O_2 \rightarrow 2FeO$$
$$MnO + SiO_2 \rightarrow MnSiO_3$$
$$FeO + SiO_2 \rightarrow FeSiO_3$$

Carbon mostly present in the form of Fe_3C reacts with FeO and O_2.

$$FeO + Fe_3C \rightarrow 4Fe + CO$$
$$2Fe_3C + O_2 \rightarrow 6Fe + 2CO$$

The evolved CO reacts with oxygen of the blast to form CO_2 and a blue flame is observed at the mouth of the converter. As soon as the blue flame dies down it is evident that all the carbon has been oxidised and the blast of air is turned off. At this stage the converter is tilted and requisite amount of carbon (in the form of charcoal) alongwith manganese (in the form of spiegeleisen : 15-20% Mn and the rest iron) is added to the molten iron. Most of the manganese is oxidised to MnO thus removing any oxygen in the iron. The added carbon brings the level of carbon to that desired of the steel. Bessemer operation gives a steel of the approximate composition : Fe 98.4%, C, 0.4%, Mn 0.9%. P 0.1%, Si 0.1%). While in the molten state the Bessemer steel is poured into moulds and high quality pipes, tubes, etc, are made.

The Lintz and Donawitz (L. D.) Process : The nitrogen present in the air blast during the Bessemer process badly affects the mechanical properties of the steel. In the L. D. process a blast of nearly pure oxygen is blown into the molten pig iron from the top. Impurities like sulphur, phosphorus are quickly oxidised. Oxidation of the carbon can also be regulated through quick analyses. This process gives better quality steel than the Bessemer method.

2. *Open Hearth process* : The hearth meant for purification of the pig iron from the blast furnace is a shallow one (Fig. 23.5). The hearth is covered with a roof through which oxygen is introduced onto the hearth. The hearth is made of pig iron but it has an inner lining of an acidic or basic material depending on the composition of the pig iron. If the pig iron contains sulphur or phosphorus the lining is made of basic lime and magnesia (CaO/MgO). On the other hand if the pig iron contains basic impurities the inner lining of the hearth consists of refractory silica. In practice most open hearths have a basic lining so that the silicon, phosphorus, sulphur, etc-can react with oxygen and the lining of the hearth to form suitable slag. The hearth is flanked on either side by two *checker chambers* which are series of passages made of firebrick. The fuel gases, consisting of producer gas, coal gas and sufficient air, are taken out alternatively through the checker chambers. The fuel gases follow the spent gases through the checkers and are thus preheated prior to combustion. This economises on fuel.

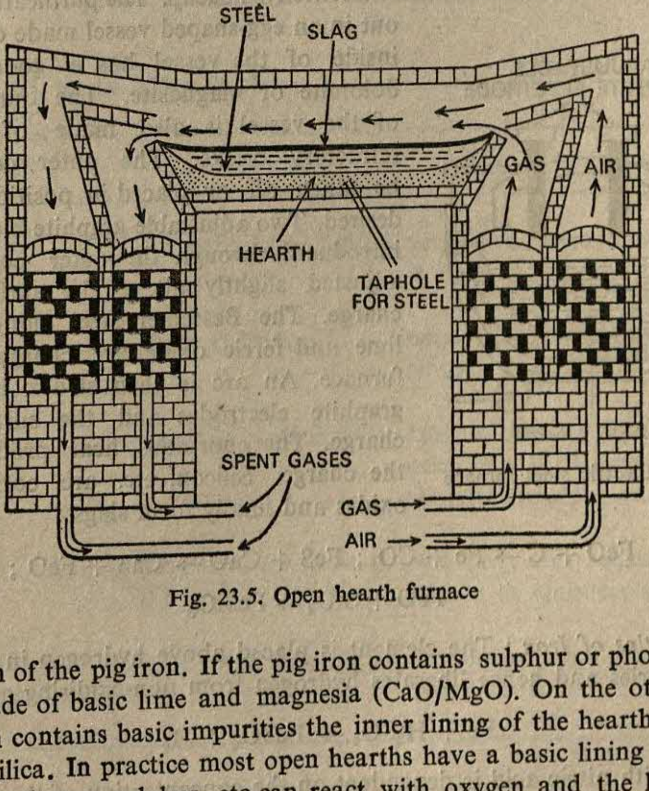


Fig. 23.5. Open hearth furnace

The hearth is fed with pig iron fresh from the blast furnace. Alongwith the pig iron some Fe_2O_3 and scrap iron are also added. Silicon, manganese and phosphorous are easily converted to slags : $CaSiO_3$, $MnSiO_3$, $FeSiO_3$, $Ca_3(PO_4)_2$. The excess carbon in pig iron is slowly oxidised to CO which helps to keep the molten charge in stirred condition.

$$2C + O_2 \rightarrow 2CO \; ; \; 3Fe_3C + Fe_2O_3 \rightarrow 11Fe + 3CO$$

In this process the purification continues slowly and the steel can be withdrawn from time to time to follow the process of purification and corrective measures adopted. Although the open hearth process is slow it gives better quality steel compared to the Bessemer process.

III. ELECTRIC HEATING PROCESS : This process of making steel is costly and is applicable to those countries where electricity is cheap. The purification is carried out in an egg-shaped vessel made of steel. The inside of the vessel has a good lining of dolomite or magnesite. The outer covering of the vessel is also made of steel and refractory bricks. The outer covering can be taken off or placed in position whenever desired. Two adjustable graphite electrodes are introduced through the outer covering and adjusted slightly above the surface of the charge. The Bessemer steel alongwith some lime and ferric oxide are charged into this furnace. An arc is then struck between the graphite electrodes and the surface of the charge. The enormous heat produced melts the charge. Silicon, etc. are converted into oxides and finally form slags :

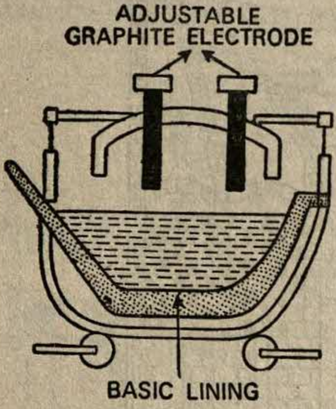


Fig. 23.6. Electric steel furnace

$$FeO + C \rightarrow Fe + CO \; ; \; FeS + CaO \rightarrow CaS + FeO \; ;$$

$$FeO + SiO_2 \rightarrow FeSiO_3$$

Properties of Iron : The element is placed above hydrogen in the electrochemical series and hence liberates hydrogen from non-oxidising acids :

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

Reaction with nitric acid is dependent on the concentration of the acid as well as the temperature :

with dilute HNO_3 at ordinary temperature :

$$4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

with hot and concentrated HNO_3 :

$$Fe + 6HNO_3 \rightarrow Fe(NO_3)_3 + 3NO_2 + 3H_2O$$

Red hot iron reacts with steam to produce hydrogen and ferroso-ferric oxide :

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

The metal reacts with dry chlorine to give anhydrous $FeCl_3$:

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

Alloy Steels : Modern developments in technology and science, in nuclear power, in every aspect of life have led to an increasing demand for stronger, rust- and heat-resistant, more flexible and lightweight alloy steels. Ordinary steel is an alloy of iron and carbon. Incorporation of some transition metals in right proportions have produced alloy steels of desired properties. Alloy steels are made in *electric arc furnaces* where temperature and the atmosphere are carefully controlled to produce the high quality steels. Table 23.4 gives the approximate composition, properties and uses of some important alloy steels.

Table 23.4. Some Alloy Steels

Alloying metal	Composition	Properties and Uses
Manganese	$>10\%$ Mn; $1.0 - 1.4\%$C	very hard; used in rails, chains, in making crushers
Nickel	3% Ni ; 0.3%C	used in making propellers, moulds of steel
Chromium	$4 - 10\%$Cr ; $<0.2\%$C	rust-resistant ; increases hardness ; used in machines operating at high temperature and pressure
Chromium and nickel	17-19% Cr ; 7-9% Ni ; $\sim 0.2\%$ C	extremely rust-resistant ; known as stainless steel
Tungsten and chromium	18% W ; 4% Cr ; 1% C	extremely tough ; used in high speed tools

COBALT

23.7.1. Trivalent Cobalt : Trivalent cobalt is most known in its many many thousand coordination complexes. Only a few relatively simple compounds are known.

Cobaltic sulphate and alum : Cobaltous sulphate can be oxidised anodically to the cobaltic sulphate. In a diaphragmed cell a solution of cobaltous sulphate in $10N H_2SO_4$ serves as the anolyte while $10N$ H_2SO_4 functions as the catholyte. Temperature is maintained below 10°C. Platinum electrodes and a high current density are used. Greenish blue crystals of $Co_2(SO_4)_3.18H_2O$ are obtained in the anode chamber.

During the above electrolysis if the anolyte contains in addition ammonium or potassium sulphate then deep blue crystals of cobaltic alums are obtained in the anode chamber : $NH_4(K)Co(SO_4)_2.12H_2O$. Trivalent cobalt can oxidise iodide ion to iodine :

$$2Co^{3+} + 2I^- \rightarrow 2Co^{2+} + I_2$$

This oxidation of the iodide ion is not possible by strong cobalt (III) complexes as the cobaltic ion is strongly complexed by other groups and thus free cobalt (III) ion is not available for the oxidation.

Cobaltic Oxide : This is obtained on oxidation of a cobaltous solution by hypochlorite or hydrogen peroxide in alkaline medium. Black coloured Co_2O_3 is precipitated. It liberates iodine from acidified KI :

$$Co_2O_3 + 2KI + 6HCl \rightarrow 2CoCl_2 + 2KCl + I_2 + 3H_2O$$

Hexammine cobalt (III) chloride : This is one of the earliest complexes of trivalent cobalt. This is nowadays prepared very readily by aerial oxidation of a mixture of $CoCl_2$, NH_4Cl, NH_4OH in the presence of active charcoal as a catalyst. After the oxidation is over (about 2 hours) the mixture is filtered. The cobalt hexammine chloride alongwith the charcoal is dissolved in minimum water and filtered. The filtrate on standing gives the orange crystals of $[Co(NH_3)_6]Cl_3$. Charcoal acts as a catalyst by restricting the formation of other complexes like $[Co(NH_3)_5 Cl] Cl_2$ etc.

$$2CoCl_2 + 2NH_4Cl + 10NH_3 + \tfrac{1}{2}O_2 \rightarrow 2[Co(NH_3)_6]Cl_3 + H_2O$$

Sodium Cobaltinitrite : This is obtained as yellow powder by oxidising a mixture of $CoCl_2$, $NaNO_2$ and acetic acid by a stream of air :

$$CoCl_2 + 7NaNO_2 + 2CH_3COOH + \tfrac{1}{2}O_2 \rightarrow Na_3[Co(NO_2)_6]NO_2 + H_2O + 2NaCl + 2CH_3COONa$$

Potassium ion can be gravimetrically estimated by this reagent as the potassium cobaltinitrite is insoluble in water.

23.7.2. Bivalent Cobalt : Several simple compounds of bivalent cobalt are known. For most of these the starting materials are cobaltous oxide and cobaltous carbonate.

Cobaltous Oxide : This is precipitated as a gelatinous green precipitate on the addition of an alkali. NaOCl, H_2O_2 or bromine can oxidise this oxide to the cobaltic stage, Co_2O_3. This is almost black in colour. Dry Co_2O_3 may be reduced by hydrogen under heating to get pure CoO. This is gray looking.

Cobaltous Carbonate : $CoCO_3.6H_2O$ is precipitated as light violet product on treating a cobaltous salt solution with $NaHCO_3$ and CO_2. The anhydrous cobalt carbonate is formed on using Na_2CO_3 instead of $NaHCO_3$.

Cobaltous Chloride : Cobaltous oxide or carbonate is dissolved in aqueous HCl and the solution concentrated to get rose coloured crystals of $CoCl_2.6H_2O$. The anhydrous blue $CoCl_2$ is obtained when the hydrated salt is heated with thionyl chloride $SOCl_2$. The colour of the aqueous solution of cobaltous chloride is light rose-red. On the addition of excess HCl the colour changes to deep blue due to the formation of tetrahedral $[CoCl_4]^{2-}$. The rose-red colour is due to the hexaaquo octahedral $[Co(H_2O)_6]Cl_2$. Anhydrous blue $CoCl_2$ is mixed with silica gel to serve as an indicator when the latter is used as dehydrating agent. On absorption of sufficient water the colour changes to rose and at this stage the silica gel is reheated to the blue form and reused as the dehydrating agent.

Cobalt Sulphate : This compound is formed on dissolving coabaltous oxide or carbonate in dilute sulphuric acid. The rose coloured solution is concentrated when $CoSO_4.7H_2O$ crystallises. This is a true vitriol. It combines with monovalent sulphates to form double sulphates of the schonite series : $(NH_4)_2SO_4.CoSO_4.6H_2O$. This double sulphate is isomorphous with other double sulphates of the schonite series.

Cobalt Nitrate : Cobaltous oxide or the nitrate is dissolved in nitric acid. The solution is next concentrated to get rose-red crystals of $Co(NO_3)_2.6H_2O$. This compound is used in the qualitative detection of some metal ions. Mixed oxides of cobalt (II) and zinc (II) or aluminium (III) have characteristic colours. Zinc or aluminium salts are heated on a charcoal block with a blow pipe. Thereafter a drop or two of the cobalt nitrate solution is added and heated again on the charcoal block with a blow pipe :

$$2Co(NO_3)_2 \rightarrow 2CoO + 4NO_2 + O_2$$

$$CoO + Al_2O_3 \rightarrow CoAl_2O_4 \text{ (blue ; known as Thenard's blue)}$$

$$CoO + ZnO \rightarrow CoZnO_2 \text{ (green ; known as Rinmann's green)}$$

22.7.3. Extraction of Cobalt : In nature cobalt is always found with arsenic and sulphur. Several other metals are also associated with cobalt ores. These metals are nickel, copper, silver and iron. The major ores are smaltite ($CoAs_2$), cobaltite (CoAsS), erythrite ($3CoO.As_2O_3.8H_2O$ i.e $Co_3(AsO_4)_2.8H_2O$). Extraction involves a series of chemical reactions. A flowsheet diagram is given to indicate the different steps involved in the extraction process (Fig. 23.7)

Uses : Cobalt forms a very important constituent of alloy steel. Stellite, a cobalt containing alloy steel, forms excellent surgical instruments. It is rust —resisting and is extremely tough. The stellite also contains tungsten, nickel, chromium, molybdenum. In the construction of permanent magnets besides iron, cobalt and nickel are also used. Cobalt-60 isotope emits both beta rays and gamma rays. The beta emission is absorbed by steel shields and the emitting gamma rays are used in radiotherapy. Cobalt-60 is also used in preservation of food stuff.

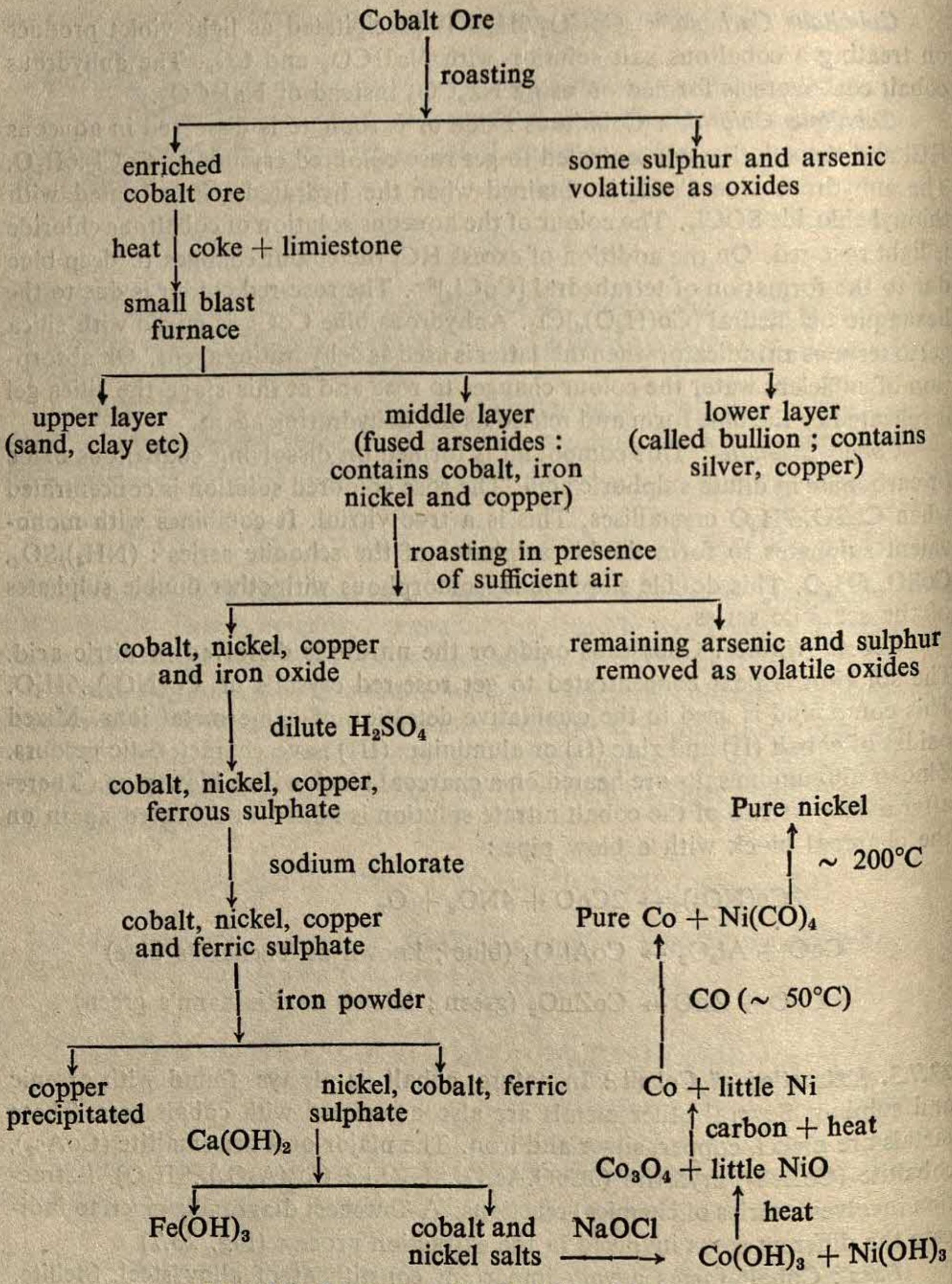

Cobalt Ore
roasting
enriched cobalt ore
some sulphur and arsenic volatilise as oxides
heat
coke + limiestone
small blast furnace
upper layer (sand, clay etc)
middle layer (fused arsenides : contains cobalt, iron nickel and copper)
lower layer (called bullion ; contains silver, copper)
roasting in presence of sufficient air
cobalt, nickel, copper and iron oxide
remaining arsenic and sulphur removed as volatile oxides
dilute H_2SO_4
cobalt, nickel, copper, ferrous sulphate
sodium chlorate
cobalt, nickel, copper and ferric sulphate
iron powder
copper precipitated
nickel, cobalt, ferric sulphate
$Ca(OH)_2$
$Fe(OH)_3$
cobalt and nickel salts
NaOCl
$Co(OH)_3 + Ni(OH)_3$
heat
Co_3O_4 + little NiO
carbon + heat
Co + little Ni
CO (~ 50°C)
Pure Co + $Ni(CO)_4$
~ 200°C
Pure nickel

Fig. 23.7. Recovery of cobalt from its ore

NICKEL

23.8.1. Bivalent Nickel : A few complicated complexes of quadrivalent and trivalent nickel are quite well known. In this section we shall deal with a few of the more important and common bivalent nickel compounds.

Nickel Oxide : Hydroxide of bivalent nickel is precipitated as a green mass $Ni(OH)_2$. The hydroxide is converted to NiO on heating the green hydroxide in the absence of air.

Nickel Sulphate : This is obtained on dissolution of nickel carbonate, nickel hydroxide or nickel oxide in sulphuric acid. On concentration and cooling the vitriol $NiSO_4.7H_2O$ crystallises from solution. This also combines with monovalent sulphates to give double sulphates of the schonite series : $(NH_4)_2SO_4.NiSO_4.6H_2O$. On strong heating the sulphate decomposes :

$$NiSO_4 \xrightarrow{\text{heat}} NiO + SO_3$$

Nickel Chloride : This is obtained by the action of HCl on nickel hydroxide or nickel carbonate. On concentration and cooling crystals of $NiCl_2.6H_2O$ are formed. On careful heating it first gives the anhydrous chloride (yellow) which decomposes in air to NiO :

$$\underset{\text{(green)}}{NiCl_2.6H_2O} \xrightarrow{\text{heat}} \underset{\text{(yellow)}}{NiCl_2} + 6H_2O$$

$$2NiCl_2 + O_2 \rightarrow 2NiO + 2Cl_2$$

The anhydrous chloride is also obtained by heating the hydrated salt with thionyl chloride. It gives a double chloride with ammonium chloride :

$$NH_4Cl + NiCl_2.6H_2O \rightarrow NiCl_2.NH_4Cl.6H_2O$$

Nickel Nitrate : Using HNO_3 and nickel hydroxide or carbonate one can prepare this salt : $Ni(OH)_2 + 2HNO_3 \rightarrow Ni(NO_3)_2 + 2H_2O$. The compound crystallises with six molecules of water : $Ni(NO_3)_2.6H_2O$. It is as usual a green compound. On heating this decomposes to NiO :

$$2Ni(NO_3)_2 \rightarrow 2NiO + 4NO_2 + O_2$$

The hydrated salt can be rendered anhydrous by heating in an atmosphere of N_2O_5 : $Ni(NO_3)_2.6H_2O + 6H_2O_5 \rightarrow Ni(NO_3)_2 + 12HNO_3$

Nickel Carbonyl : This is a tetracarbonyl of zerovalent nickel. The compound $Ni(CO)_4$, is made use of in obtaining nickel free from cobalt. At about 50°C under ordinary pressure metallic nickel reacts with CO to form colourless liquid $Ni(CO)_4$. The compound decomposes at about 200°C to give very pure nickel. Cobalt does not react with CO under these conditions to give a carbonyl.

23.8.2. Extraction of Nickel : Nickel is found in nature in combination with arsenic and sulphur. Some of the important nickel bearing minerals are nickelite $(NiAs_2)$, garnerite $(Ni, Mg)SiO_3.xH_2O$, pentlandite $(Ni,CuFe)S$. Heaviest concentration of nickel ore is at Sudbury in Ontario, Canada. This Sudbury ore contains nickel sulphide alongwith sulphides of copper and ferrous iron. Fig. 23.8 gives a flowsheet of the different steps involved in the recovery of nickel from Sudbury ores.

Uses of Nickel : The major use of nickel is in the preparation of various alloy steels (Table 23.5). Nickel also finds use as a catalyst in hydrogenation of fats and oils.

Table 23.5. Alloy Steels containing Nickel

Name of the steel	Composition	Uses
Stainless steel	17-19% Cr; 7-9% Ni ; 0.2%C	mostly in utensils
German silver	25-50% Cu; 25-25% Zn; 35-10% Ni	utensils, ornament
Monel metal	67% Ni ; 30% Cu ; little Fe	used as substitute of steel
Nichrome	60% Ni ; 14% Cr ; 24% Fe	coils of electrical furnaces

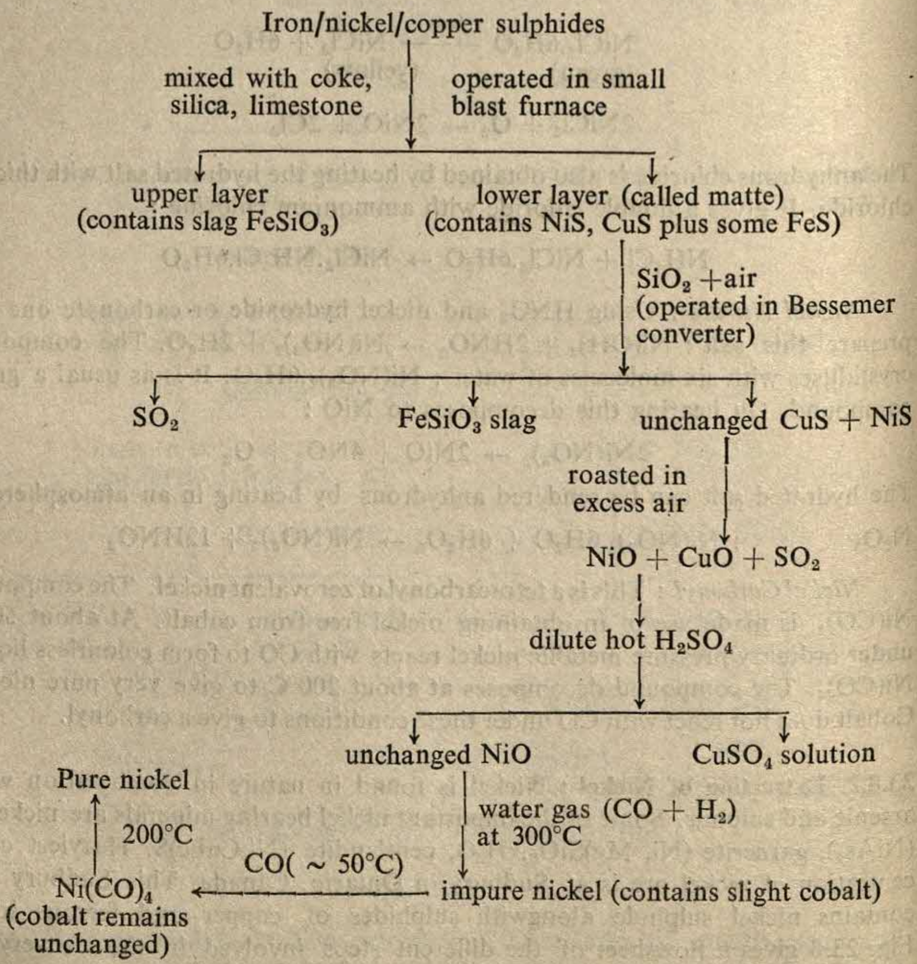

Iron/nickel/copper sulphides
mixed with coke, silica, limestone
operated in small blast furnace
upper layer (contains slag $FeSiO_3$)
lower layer (called matte) (contains NiS, CuS plus some FeS)
SiO_2 +air (operated in Bessemer converter)
SO_2
$FeSiO_3$ slag
unchanged CuS + NiS
roasted in excess air
NiO + CuO + SO_2
dilute hot H_2SO_4
unchanged NiO
$CuSO_4$ solution
water gas (CO + H_2) at 300°C
impure nickel (contains slight cobalt)
CO(~ 50°C)
$Ni(CO)_4$ (cobalt remains unchanged)
200°C
Pure nickel

Fig. 23.8. Recovery of nickel from Sudbury ore

EXERCISES

1. Define and distinguish representative and transition elements. Would you include both copper and zinc within the family of transition elements?

2. Taking chromium as a typical element explain how the acid character and base character change with changing oxidation number.

3. Pick out the acidic and basic oxides from the list and give supporting reasons :

FeO, NiO, FeO_3, CrO_3, MnO, Mn_2O , Cr_2O_3, Fe_2O_3.

4. Point out the merits and demerits of $KMnO_4$ and $K_2Cr_2O_7$ as oxidising reagents.

5. Present a concise resume of the chemistry of iron, cobalt and nickel.

6. Write a connected account of vitriols, schonites and alums. Does lithium form any alum?

7. Write short notes on the following compounds :
(*a*) potassium ferrocyanide (*b*) potassium dichromate (*c*) chrome alume (*d*) chromous acetate (*e*) Mohr's salt (*f*) sodium nitroprusside (*g*) nickel carbonyl (*h*) sodium cobaltinitrite (*i*) potassium ferrate (*j*) potassium ferrocyanide (*k*) Prussian blue and Turnbull's blue (*l*) anhydrous cobalt chloride (*m*) anhydrous ferric chloride

9. What constitutes the blast furnace charge? Give an account of the reactions that take place inside the blast furnace.

10. Give an idea of the extraction of nickel from Sudbury ore.

11. Give a comparative account of the Bessemer process and the open hearth process.

12. Complete the following reactions :

(*a*) $CrO_3 + H_2S + H_2SO_4 \rightarrow$
(*b*) $K_2Cr_2O + KI + H_2SO_4 \rightarrow$
(*c*) $CrO_3 + HCl \rightarrow$
(*d*) $CrCl_2 + HCl + O_2 \rightarrow$
(*e*) $KMnO_4 + H_2SO_4 + H_2O_2 \rightarrow$
(*f*) $KMnO_4 + H_2O + KI \rightarrow$
(*i*) $FeSO_4 + H_2SO_4 + MnO_2 \rightarrow$
(*j*) $K_4[Fe(CN)_6] + KMnO_4 + HCl \rightarrow$

CHAPTER 24

GROUP IB : COPPER, SILVER AND GOLD

24.1. INTRODUCTION

In the original Mendeleev periodic table we find the alkali metals occupying group IA while copper, silver and gold occupied group IB. Later in the long form periodic table the two subgroups were widely separated from each other. Subgroups A and B were placed on either side of the group VIII. Placing the two subgroups in the same column by Mendeleev were not without any justification but later on with more of their chemistries coming up it was realised that there were more dissimilarities between the two subgroups than there were similarities. So today we find that it has been wiser to accept the long form periodic table arrangement. We must not lose sight of the electronic configuration of these elements. While the alkalies are representative elements, copper, silver and gold, the so called coinage metals, belong to the family of the transition elements.

24.2. A RESUME OF THE CHEMISTRY OF COPPER SILVER AND GOLD

Table 24.1 records some of the physical characteristics of these three elements. If we look into the ground state electronic configuration of these elements they will

Table 24.1. Some Properties of Copper, Silver and Gold

Element	Atomic Number	Electron Distribution	Ionisation Potential (*ev*)	Electro negativity	Atomic Radius (A)	M.P (°C)	E° (volt) $M^+ + e \rightleftharpoons M$
Cu	29	$[Ar]3d^{10}4s^1$	7.72	1.9	1.28	1083	0.52
			20.29				
			36.83				
Ag	47	$[Kr]4d^{10}5s^1$	7.57	1.9	1.43	960	0.79
			21.48				
			34,82				
Au	79	$[Xe]4f^{14}5d^{10}6s^1$	9.22	2.4	1.44	1063	1.68

be classified as representative elements. But in their bivalent or trivalent states the ions have incompletely filled *d* orbitals. So according to the accepted definition these three elements are considered as transition elements. In keeping with the tradition of transition elements they all show variable valence :

copper : +3 +2 +1
silver : +3 +2 +1
gold : +3 +1

For copper both monovalent and bivalent states are common, while for silver only the monovalent state and for gold both monovalent and trivalent states are common. For copper and silver the higher oxidation states have been stabilised through complex formation. The complexing ligands surround the metal ions in their higher oxidation states like garlands and thus impart some stability. Although both copper and silver are known in the bivalent states, gold is not. For bivalent gold the unpaired electron of the $5d^9$ level will be situated at a much higher energy and will be prone to oxidation. A second hypothetical bivalent gold can take up this electron and may get reduced to the monovalent state. Thus the reality is that bivalent gold is so very readily disproportionated to two different valence states: one higher and the other lower:

$$2Au^{2+} \rightarrow Au^{3+}\ (5d^8) + Au^{+}\ (5d^{10})$$

One other interesting feature of their chemistry is their reduction potential. The reduction potentials of all these three elements are positive and increase very substantially from copper to gold. This means that the reducing ability of the metals decreases very substantially from copper to gold. In other words it is far easier to reduce monovalent gold ion to metallic gold than it is for monovalent copper to elementary copper.

Chemical Properties: Cuprous oxide is unstable. Usually in alkaline medium the cupric oxide is reduced by hydrogen to the yellow cuprous oxide. Cuprous compounds are readily oxidised in air with the exceptions of a few (like CuI, CuSCN). Alkali precipitates brown black Ag_2O from solutions of silver (I). This oxide can be oxidised to black AgO by NaOCl or $Na_2S_2O_8$. This so called AgO is a mixed compound of Ag_2O and Ag_2O_3 (= 4AgO). Addition of magnesia to auric compounds gives $Mg(AuO_2)_2$, which on acidification gives AuO.OH. In KOH the gold oxide hydroxide gives $KAuO_2$ or $K[Au(OH)_4]$. In general the trivalent oxides are acidic, the monovalent oxides are basic while the bivalent ones are somewhat amphoteric.

Cuprous halides are normally prepared by the reduction of cupric halides by metallic copper. Cuprous iodide is very stable but the chloride is readily oxidised by air. Monovalent silver halides are quite stable probably because of their insolubility. AgF is soluble in water but for the other three solubility decreases from chloride to the iodide. For the cupric state, the iodide is unknown but the other three halides are quite well known. AgF_2 is known and is used in fluorination of many organic compounds. Auric chloride is dimeric in nature and has chlorine bridges. Anhydrous cupric chloride is polymeric through chlorine bridges.

Typical of transition elements, compounds of these elements are of varied colours. Depending on the oxidation state and the nature of the compound we find both para- and diamagnetism in their compounds (Table 24.2).

Table 24.2. Some Compounds of Copper, Silver and Gold

Element	Oxidation State	Compounds	Colour	Magnetic Properties
Copper	+ 1	CuI, CuSCN	colourless	diamagnetic
	+ 2	$CuSO_4.5H_2O$	Blue	paramagnetic
Silver	+ 1	$AgNO_3$	colourless	diamagnetic
	+ 2	$[Ag(pyridine)_4] (NO_3)_2$	orange	paramagnetic
Gold	+ 1	AuCl	light yellow	diamagnetic
	+ 3	$(AuCl_3)_2$	deep red	diamagnetic

24.3. A COMPARISON OF GROUP IA AND IB ELEMENTS

Group IA elements comprise lithium, sodium, potassium, rubidium and caesium while group IB elements are copper, silver and gold. The electronic configurations of two elements from the two subgroups are shown below:

Potassium: atomic number 19: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

Copper : atomic number 29: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Both the elements have one electron in their outermost *s* orbital. But in the case of potassium and the other alkali metals below the outermost *s* electron there lie the stable electron core of the noble gases. In the case of copper and the other two coinage elements below the outermost *s* electron we find a saturated *d* level. Since the noble gas electronic core is a very stable one we find that the alkali metals cannot lose more than one electron for valence purpose. On the other hand in the case of the group IB elements not only the *s* electron but also one or more electrons from the *d* level can be utilised for valence purpose. Thus the alkalies are consistently monovalent but the coinage metals show variable valence (+3, +2 and +1). To sum up the group IA elements are representative elements while the group IB elements are transition elements. Characteristic of representative elements compounds of the alkalies are colourless and diamagnetic but those of the coinage elements are coloured and show magnetism of varied types (Table 24.2).

As expected the ionisation potentials of the group IA elements are small and decrease further with increasing atomic number. But this is not so in group IB. There is no regular trend in the variation of the ionisation potentials in group IB. More interesting is a comparison of the reduction potentials. In group IA the reduction potentials are distinctly negative and become more and more negative from sodium to caesium, This tells us that the reducing capacity of the elements increase with increasing atomic number. This also tells us that it becomes more and more difficult to reduce their ions to the metallic state. On the contrary the reduction potentials of the group IB elements are positive and that again the positive values become more and more positive as we move from copper to gold. Thus we see the reverse trend holds here: with increasing atomic number from copper to gold it becomes more and more easy to reduce their ions to the elementary state. This explains why we often find gold native in nature.

In the electrochemical series the alkalies are placed much above hydrogen and as a result the alkalies displace hydrogen from even as weak an acid as water. On the other hand the group IB elements are below hydrogen in the electrochemical series and hence cannot evolve hydrogen from acids.

The electronegativities of the group IA elements are around 1.0 whereas those of the group IB are in the range 1.9 to 2.4. The alkalies therefore very readily form ionic compounds but the coinage elements mostly give covalent and complex compounds.

Since the alkalies form very stable cations it is hard to reduce them to the corresponding metals. Electrolysis of the fused halides is the only way out. For the coinage elements other cheaper methods of extraction are available (Chapter 13).

COPPER

24.4.1. Trivalent Copper : This is an unusual oxidation state of copper. Only three compounds have so far been characterised with copper in this higher oxidation state. It can be guessed that those complexing ligands which have no chance of themselves being oxidised further are the best ones for complexation and stabilisation of this unusual higher oxidation state. Periodate ion, IO_6^{5-}, and tellurate ion, TeO_6^{6-}, have their central element iodine and tellurium already in their respective highest oxidation state. Oxidation of copper (II) by potassium peroxydisulphate in the presence of the above stabilising ions gives maroon red crystals of compounds of the type $K_7[Cu(IO_6)_2].7H_2O$, $Na_7H_2[Cu(TeO_6)_2].12H_2O$. Two oxygens from each of the two octahedral IO_6^{5-} and TeO_6^{6-} ions give a square planar geometry around copper (III). Besides these two complexes a hexafluoro complex has also been reported. A mixture of KCl and anhydrous $CuCl_2$ has been oxidised by fluorine to give green coloured $K_3[CuF_6]$.

24.4.2. Bivalent Copper : This is the common and commercially available state of copper. A very large number of complexes are known. We shall restrict our discussion only to some simple type compounds.

Cupric Chloride: The anhydrous compound is obtained by the passage of dry chlorine gas over copper powder. From aqueous solution it may be crystallised as the dihydrate: $CuCl_2.2H_2O$. Its aqueous solution is coloured green but in the presence of a large amount of chloride ion gives yellowish green tetrahedral $[CuCl_4]^{2-}$.

Cupric Bromide: This is obtained as dark coloured anhydrous $CuBr_2$ by the action of bromine on metallic copper. The tetrahydrate, $CuBr_2.4H_2O$, crystallises as dark green product from aqueous solution.

Cupric Nitrate: This is obtained by the straight forward reaction between metallic copper and nitric acid. It crystallises from aqueous acid as the hexahydrate $Cu(NO_3)_2.6H_2O$:

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Cupric Sulphate: This is the most important of all the cupric compounds. It is formed by the reaction of copper and sulphuric acid in the presence of air.

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O$$

For commercial level preparation a lead lined chamber is filled with scrap copper. Sulphuric acid is allowed to flow in as a spray from the top while steam and air are forced through the bottom. The copper sulphate solution is collected through a side tube at the lower portion and is recycled through the top. On crystallisation we get $CuSO_4.5H_2O$. This has been called *blue vitriol*. But the real vitriols are bivalent metal sulphates crystallising with seven molecules of water. On careful dehydration at about 100°C light blue monohydrate $CuSO_4.H_2O$ is obtained and at about 200°C the anhydrous colourless $CuSO_4$ results. It is however very difficult to get the anhydrous compound without decomposition. On strong heating the compound breaks up into CuO and SO_3.

Cupric Acetate: This is prepared by treating cupric carbonate with acetic acid. On concentration glistening crystals of the acetate salt are obtained. The compound is known to be a dimer: $[Cu(CH_3COO)_2.H_2O]_2$. Its structure is parallel to that of chromous acetate (Chapter 23, Fig. 23.2) Each of the two acetate ions functions as a bridging bidentate OO donor and is bonded to the two copper atoms.

Basic Cupric Acetate: Acetic acid reacts with copper plates in an atmospheer of air to give the green coloured basic acetate:

$$Cu + CH_3COOH + \tfrac{1}{2}O_2 \rightarrow (CH_3COO)CuOH$$

This is commercially known as *verdigris* and is used as a pigment.

24.4.3. Monovalent Copper : There are some stable cuprous compounds. Of these cuprous iodide and cuprous thiocyanate play important role in the quantitative determination of copper.

Cuprous Oxide: This oxide is red in colour and can be obtained by several methods: (1) by reduction of CuO by copper under heating (2) by heating CuO alone and (3) by reduction of cupric salt in alkaline medium by glucose.

Cuprous Halides: Cuprous chloride is formed on heating a solution of cupric chloride and HCl with copper turnings. The green colour of the cupric ion is gone and the solution turns colourless. This solution is added to a solution of SO_2 when cuprous chloride, CuCl, is precipitated. This may be filtered, washed with alcohol and ether and stored in a stoppered container. Ammoniacal cuprous chloride is a good absorbent for CO. CuCl.CO is thereby produced. Cuprous chloride is a trimeric triangular compound. The three chlorines form bridges among the three copper atoms. Similar reduction of cupric bromide ($CuBr_2 + Cu \rightarrow 2CuBr$) gives light yellow CuBr. Cuprous iodide is readily precipitated on the addition of KI to any cupric solution. This is colourless and air stable Formation of insoluble CuI on the addition of KI to a copper (II) solution alongwith the liberation of iodine is taken advantage of in the volumetric (iodometric) determination of copper. The liberated iodine is titrated by a standard solution of sodium thiosulphate using starch as indicator:

$$CuSO_4 + 2KI \rightarrow CuI + K_2SO_4 + \tfrac{1}{2}I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Therefore $Cu^{2+} \equiv I \equiv Na_2S_2O_3$

$1000 \text{ ml } N\, Na_2S_2O_3 \equiv 1$ gram ion $Cu^{2+} \equiv 63.54$ gram copper

$1 \text{ ml } (N/10)\, Na_2S_2O_3 \equiv 0.006354$ gram copper

Problem 1. 10 ml of a solution contains both ferric and cupric ions. This is diluted to 250 ml. 50 ml of this solution is taken and the copper precipitated as CuS. The CuS is filtered, dissolved in dilute HNO_3, neutralised with NH_4OH and finally acidified with dilute acetic acid. Excess KI is next added and the liberated iodine titrated with a sodium thiosulphate solution. This requires 7.9 ml of the thiosulphate. 23.1 ml. of the thiosulphate is equivalent to 25 ml of $N/10$ $K_2Cr_2O_7$ solution. Calculate the total quantity of copper present in the original 10 ml of the solution.

$$\text{Strength of the } Na_2S_2O_3 \text{ solution} = \frac{25 \times 1}{23.1} = 1.082\ (N/10)$$

$$\text{Amount of copper in 50 ml of the diluted solution} = 7.9 \times 1.082 \times 0.006354 \text{ gram}$$

$$\text{Total quantity of copper} = 5 \times 7.9 \times 1.082 \times 0.006354 = 0.2716 \text{ gram}$$

Problem 2. One litre of a potassium dichromate solution contains 2.5 gram. Excess KI was added to 25 ml of this solution. On titration of the liberated iodine 30 ml of a thiosulphate solution was required. 2.5 gram of a copper alloy was dissolved in dilute H_2SO_4 and the volume was made upto 500 ml. 20 ml of this alloy solution was treated with KI and the iodine was titrated with the above thiosulphate solution. The volume of thiosulphate required was 25 ml. Calculate the percentage of copper in this alloy.

$K_2Cr_2O_7$ has two hexavalent chromiums per molecule and these are reduced to trivalent chromium. Hence its equivalent weight is:

$$\text{equivalent weight} = \frac{(2 \times 39) + (2 \times 52) + (7 \times 16)}{2 \times 3} = 49$$

$$\text{Normality of the dichromate solution} = \frac{2.5}{49} = 0.51\ (N/10)$$

$$\text{Normality of the } Na_2S_2O_3 \text{ solution} = \frac{0.51 \times 25}{30} = 0{,}425\ (N/10)$$

Amount of copper in 20 ml of the alloy solution

$$= 25 \times 0.425 \times 0.006354 = 0.06751 \text{ gram}$$

Amount of copper in 500 ml of the alloy solution $= \frac{0.06751 \times 500}{20}$

$$= 1.6877 \text{ gram}$$

Percentage of copper in the alloy $= \frac{1.6877 \times 100}{2.5} = 67.5\%$

Cuprous Thiocyanate: This compound, CuSCN, is precipitated as a white product on the addition of ammonium thiocyanate (NH_4SCN) to a solution of cuprous copper, obtained by the reduction of cupric copper by sulphur dioxide.

$$2CuCl_2+SO_2+2NH_4SCN+2H_2O \rightarrow 2CuSCN+2NH_4Cl+H_2SO_4+2HCL$$

The precipitate of CuSCN is quantitative and hence copper is quantitatively estimated as cuprous thiocyanate.

Cuprous Cyanide: The blue colour of a cupric solution is discharged on the addition of KCN due to reduction to cuprous copper which forms cuprocyanide complex on the addition of excess KCN:

$$CuSO_4 + 2KCN \rightarrow Cu(CN)_2 + K_2SO_4$$

$$2Cu(CN)_2 \rightarrow 2CuCN + C_2N_2 \text{ (cyanogen gas)}$$

$$CuCN + 3KCN \rightarrow K_3[Cu(CN)_4]$$

24.4.4. Extraction of Copper : Copper is found in nature in several forms: chalcosite, Cu_2S; copper pyrites, $Cu_2S.Fe_2S_3/CuFeS_2$; cuprite, Cu_2O; malachonite, CuO and malachite, $CuCO_3.Cu(OH)_2$.

In practice copper is extracted from copper pyrites. The raw ore is first concentrated by the froth floatation process (Chapter 13). The powdered ore is mixed with some pine oil and water and the mixture agitated with a stream of air. This causes enough frothing which carries the pyrites while clay and other siliceous matter settle down. The froth is separated and the enriched pyrites ore collected. In Fig. 24.1 is given a flow sheet diagram of the different steps involved in the extraction process.

PURIFICATION OF COPPER: The copper obtained by the procedure described in Fig. 24.1 is about 98% pure. When the fused copper cools down the trapped SO_2 comes out from within and during this evolution of SO_2 scars or blisters are left on the surface of the solid copper. The copper obtained as above is called *blister copper*. Purification of blister copper is carried out in two steps:

1. *Roasting*: Blister copper carries some small amount of sulphur and arsenic. This copper is roasted in a furnace in a stream of air. This helps in the removal of sulphur and arsenic as their oxides. Little iron and tin float above the copper and is removed. Thereafter the copper is reacted with some coke which leads to the reduction of any cuprous oxide to metallic copper.

2. *Electrolysis*: The copper as purified above is subjected to the ultimate purification via electrolysis. Blister copper as roasted above is made into plates,

These plates of slightly impure copper are suspended in a lead lined tank containing dilute H_2SO_4 and copper sulphate. These copper plates act as anodes while plates. of pure copper coated with graphite powder are made the cathodes. During electrolysis copper metal is oxidised at the anode to copper (II) ions. These migrate to the cathode and are reduced there to metallic copper. More electropositive elements like zinc, iron, nickel remain in solution. Less electropositive elements like silver, gold remain undissolved and collect below the anode plates as anode slime. Thus very pure copper is collected from the cathode plates.

at the anode: $Cu \rightarrow Cu^{2+} + 2e$; *at the cathode:* $Cu^{2+} + 2e \rightarrow Cu$

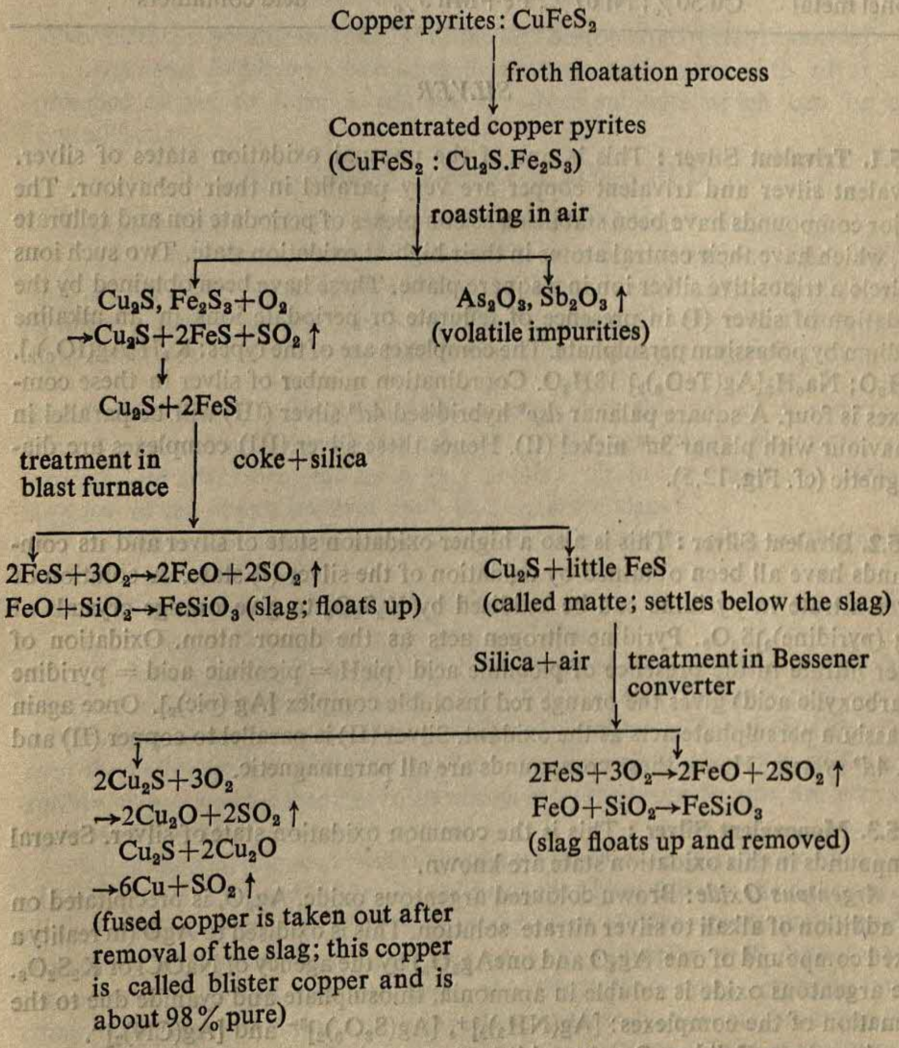

Copper pyrites: $CuFeS_2$
froth floatation process
Concentrated copper pyrites
($CuFeS_2$: $Cu_2S.Fe_2S_3$)
roasting in air
$Cu_2S, Fe_2S_3 + O_2 \rightarrow Cu_2S + 2FeS + SO_2\uparrow$
$As_2O_3, Sb_2O_3\uparrow$
(volatile impurities)
$Cu_2S + 2FeS$
treatment in blast furnace
coke+silica
$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2\uparrow$
$FeO + SiO_2 \rightarrow FeSiO_3$ (slag; floats up)
Cu_2S + little FeS
(called matte; settles below the slag)
Silica+air
treatment in Bessener converter
$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2\uparrow$
$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2\uparrow$
(fused copper is taken out after removal of the slag; this copper is called blister copper and is about 98% pure)
$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2\uparrow$
$FeO + SiO_2 \rightarrow FeSiO_3$
(slag floats up and removed)

Fig. 24.1. Flow sheet of the reactions involved in the extraction of copper from copper pyrites

Uses of Copper: It is used as conducting wires. It also finds use in a host of alloys (table 24.3.)

Table 24.3. Some Alloys of Copper

Alloy	Composition	Uses
Brass	Cu 60-80%; Zn 40-20%	utensils, cartridges
Bronze	Cu 75-90%; Sn 25-10%	coins, statues, machine
German silver	Cu 25-50%; Zn 35-25%; Ni 35-10%	utensils, ornaments
Monel metal	Cu 30%; Ni 67%; Fe+Mn 3%	acid containers

SILVER

24.5.1. Trivalent Silver : This is one of the unusual oxidation states of silver. Trivalent silver and trivalent copper are very parallel in their behaviour. The major compounds have been stabilised as complexes of periodate ion and tellurate ion, which have their central atoms in their highest oxidation state. Two such ions encircle a tripositive silver ion in a square plane. These have been obtained by the oxidation of silver (I) in presence of tellurate or periodate ions in an alkaline medium by potassium persulphate. The complexes are of the types: $K_6H[Ag(IO_6)_2].10H_2O$; $Na_6H_3[Ag(TeO_6)_2]$ $18H_2O$. Coordination number of silver in these complexes is four. A square palanar *dsp*^{2} hybridised 4*d*^{8} silver (III) will be parallel in behaviour with planar 3*d*^{8} nickel (II). Hence these silver (III) complexes are diamagnetic (cf. Fig. 12.5).

24.5.2. Bivalent Silver : This is also a higher oxidation state of silver and its compounds have all been obtained by oxidation of the silver (I) state. A solution of silver nitrate in pyridine can be oxidised by $K_2S_2O_8$ to give orange crystals of $[Ag\ (pyridine)_4]S_2O_8$. Pyridine nitrogen acts as the donor atom. Oxidation of silver nitrate in the presence of picolinic acid (picH = picolinic acid = pyridine 2-carboxylic acid) gives the orange red insoluble complex $[Ag\ (pic)_2]$. Once again potassium persulphate acts as the oxidant. Silver (II) is parallel to copper (II) and is a 4*d*^{9} system. Hence these compounds are all paramagnetic.

24.5.3. Monovalent Silver : This is the common oxidation state of silver. Several compounds in this oxidation state are known.

Argentous Oxide: Brown coloured argentous oxide, Ag_2O, is precipitated on the addition of alkali to silver nitrate solution. This is oxidised to AgO (in reality a mixed compound of one Ag_2O and one Ag_2O_3) by the agency of NaOCl or $K_2S_2O_8$. The argentous oxide is soluble in ammonia, thiosulphate and cyanide due to the formation of the complexes: $[Ag(NH_3)_2]^+$, $[Ag(S_2O_3)_2]^{3-}$ and $[Ag(CN)_2]^-$.

Argentous Halides: On the addition of the appropriate sodium halides to a solution of silver nitrate the silver halides AgCl, AgBr and AgI are precipitated, The chloride is colourless, the bromide is light yellow while the iodide is yellow in colour. The solubility of the halides in water decreases from chloride to the iodide. AgCl is readily soluble in ammonia due to the formation of $[Ag(NH_3)_2]Cl$. AgBr is soluble in good excess of ammonia but the iodide is quite insoluble. All the three halides are readily soluble in cyanide due to the formation of $[Ag(CN)_2]^-$.

Argentous Nitrate: This is obtained by dissolution of silver metal in dilute HNO_3 followed by concentration and crystallisation:

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + 2H_2O + NO$$

This is a colourless crystalline compound. It decomposes on heating:

$$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$$

Silver nitrate is soluble in water, pyridine and acetonitrile (methyl cyanide).

Argentous Sulphate: Concentrated sulphuric acid reacts with silver in the presence of air to form a solution of silver sulphate which can be easily crystallised:

$$2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + SO_2 + 2H_2O$$

Compared to the nitrate the sulphate salt is less soluble in water.

A common feature of all silver salts is their sensitiveness to light, whereby they are gradually reduced to metallic silver. Because of this property silver nitrate solution is always stored in brown bottles so as to minimise photoreduction. The light sensitiveness of silver bromide has been utilised in photography.

24.5.4. Photography : We readily take pictures with the aid of a camera and film. Behind taking snaps there works a very fine sensitive oxidation reduction process and silver bromide assumes a pivotal role in the whole art. Making a *negative* of the object involves the following three steps:

1. Exposure of the photographic film for a fraction of a second with the object in view.
2. Development of the exposed film
3. Fixing of the exposed and developed film

1. *Making of the film and its exposure*: An emulsion is made out of a solution of silver nitrate, bromide ion and gelatin. This emulsion is then laid out on a celluloid film or a glass plate. Fine particles of silver bromide are thus distributed over the entire surface of the celluloid or the glass plate. However on the upper surface many spaces, otherwise to be occupied by the bromide ions, are left vacant due to crystal defect.

When the film is loaded in the camera and the film is exposed towards a certain object for a split second light reflected from the object falls on the light sensitive silver bromide of the film. This leads to reduction of silver ion to metallic silver. It is easily understood that the extent of such reduction will depend on the intensity of the light reflected from the object. Too much exposure over a comparatively longer period will bring about total reduction of the entire silver bromide of the film and will thus destroy the entire filming. Instant exposure will provide a latent image of the object.

It is believed that the reduction of the silver ions involves the following steps:

(*a*) A photon from the reflected light removes an electron from the bromide ion: $Br^- + \gamma h \rightarrow Br + e$

(*b*) The electron so released gets into some of the defects in the upper surface of the silver bromide layer of the film.

(*c*) The above stuck-up electron initiates the reduction of the neighbouring silver ion: $Ag^+ + e \rightarrow Ag$

That area of the film which has received maximum light will have the highest concentration of silver atoms and hence will turn real black.

2. *Development of the film*: The exposed film is reacted with a *mild* reducing agent in the dark. The area over which the silver bromide particles have been sensitised gets reduced:

$$AgBr + e \rightarrow Ag + Br^- \text{ (the electron is supplied by the reducing agent)}$$

We have earlier mentioned that the exposure leads to the formation of some silver atoms in the latent image of the object. These silver atoms are believed to catalyse the above reduction process. Those areas of the film which have been least exposed to light allow the above reduction process to go slow. Because of this the film is not allowed to stay in the reducing solution for any considerable time as in that case the entire film will turn black. The best mild reducing agents for the above reduction are potassium ferrous oxalate, alkaline hydroxylamine and hydroquinone:

$$Fe^{2+} \rightarrow Fe^{3+} + e$$

$$H_2NOH + OH^- \rightarrow 2H_2O + \tfrac{1}{2}N_2 + e$$

$$\underset{\text{(hydroquinone)}}{C_6H_6O_2} \rightarrow \underset{\text{(quinone)}}{C_6H_4O_2} + 2H^+ + 2e$$

3. *Fixing of the developed film*: After development those areas of the film which have received reflected light from the object look black due to very fine silver particles. Those areas which have received no light or very little only look white because the AgBr has remained unaffected. In order to make the image a permanent one the unchanged AgBr has to be completely removed. This is done by washing the developed film with a solution of sodium thiosulphate when AgBr dissolves out of the film in the form of a soluble thiosulphate complex:

$$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

Changeover from the negative to the positive; The above negative is in fact an opposite replica of the real object. Those parts of the object which are in reality black will reflect least amount of light and hence in the negative those portions will look white or very nearly so. So the above three stages have to be reenacted taking now the negative as the object. The negative is now placed over another film and then light is allowed to pass through. Now those portions which were black in the negative will absorb more light and hence allow correspondingly less light to fall on the film. In effect we will end up with a reverse of our negative—the so called positive i.e. the real black and white photograph of the object.

24.5.5. Extraction of Silver : The main sources of silver are: argentine, Ag_2S; horn silver, AgCl; pyrargyrite (Ag_3SbS_3). Silver is mostly extracted from the sulphide ore by the cyanide method.

The sulphide ore is well powdered and treated with 1% NaCN for several hours. The mixture is agitated by air. The ore slowly reacts to give soluble sodium argentocyanide:

$$Ag_2S + 4NaCN \rightleftharpoons 2Na\,[Ag(CN)_2] + Na_2S$$

The reaction attains equilibrium. Hence to achieve maximum dissolution of the ore the Na_2S is removed as Na_2SO_4 so that the reaction can move from left to the right. This is why air is necessary. If the ore contains any AgCl then that is also worked up by the cyanide solution:

$$AgCl + 2NaCN \rightarrow Na[Ag(CN)_2] + NaCl$$

The solution of the argentocyanide is stirred with more electropositive zinc metal powder when the silver in the complex is replaced by the zinc:

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag$$

The silver so obtained is admixed with little zinc. The crude silver may be fused with KNO_3 when the zinc is oxidised while silver is left pure.

Electrorefining of impure silver: This method of purification of crude silver is parallel to that of copper. Plates of crude impure silver form anodes while plates of pure silver act as cathodes. A solution of silver nitrate act as the electrolyte. Silver from the anode passes into the solution as silver (I) ion. The silver (I) then migrates to the cathode and gets deposited on the cathode as metallic silver.

at the anode : $Ag \rightarrow Ag^+ + e$

at the cathode: $Ag^+ + e \rightarrow Ag$

Properties: Silver is placed below hydrogen in the electrochemical series and hence cannot liberate hydrogen from acids like HCl, H_2SO_4. However it dissolves in acids of oxidising ability.

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O$$

$$2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + SO_2 + 2H_2O$$

In an atmosphere of H_2S it is converted to Ag_2S with displacement of H_2:

$$2Ag + H_2S \rightarrow Ag_2S + H_2$$

Uses: It is used in coins and ornaments. It is a valuable ingredient in photography. It is also used in mirroring. Behind the glass plate of a mirror there is a fine layer of metallic silver. This fine layer is formed on reducing a solution of silver nitrate with formaldehyde:

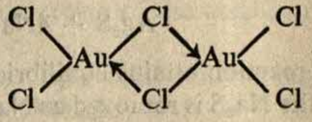
$$2AgNO_3 + HCHO + H_2O \rightarrow 2Ag + HCOOH + 2HNO_3$$

In silver plating a solution of silver nitrate and excess of NaCN is used. Silver ion dissociation from the complex Na $[Ag(CN)_2]$ is low and as a result a very coherent and stable deposit of silver is obtained on the material at the cathode.

GOLD

24.6.1. Trivalent Gold : We have already observed that bivalent gold is non-existent. Of the two oxidation states +3 and +1, the former is the more stable one.

Auric Chloride: This is obtained as dark red crystals by reacting gold with chlorine at abour 200°C. From a determination of molecular weight it is known that the compound is a dimer $(AuCl_3)_2$. Gold metal is soluble in aqua regia and gives chloroauric acid $H(AuCl_4).4H_2O$. Salts of this acid are also known (eg. $K[AuCl_4]$).



Auric Bromide: This is obtained by the reaction between gold and bromine. From a determination of molecular weight it is known to be a dimer $(AuBr_3)_2$. The gold halides decompose on heating to give gold and the halogen:

$$(AuCl_3)_2 \rightarrow 2AuCl + 2Cl_2\ ; \quad 2AuCl \rightarrow 2Au + Cl_2$$

Auric Hydroxide: A brown coloured precipitate of $Au(OH)_3$ is obtained on the addition of alkali to a solution of $K[AuCl_4]$. This hydroxide, as expected, possesses some acidic character. It dissolves in excess alkali to give the ion $Au(OH)_4^-$ or AuO_2^-. $Au(OH)_3$ reacts with ammonia to give a green coloured compound $HN = Au - NH_2.xH_2O$. On drying or slight heating it causes explosion. This is called fulminating gold.

24.6.2. Monovalent Gold : In general compounds of monovalent gold are obtained via reduction of trivalent gold compounds.

Aurous Halides: On controlled heating at about 200°C auric chloride breaks up into aurous chloride and chlorine:

$$\underset{\text{(deep red)}}{(AuCl_3)_2} \xrightarrow{200°C} \underset{\text{(yellow)}}{2AuCl + 2Cl_2}$$

Aurous bromide is obtained by a similar heating of auric bromide at ~115°C. This is coloured green. The aurous iodide is obtained by the reaction of auric chloride or potassium tetrachloroaurate with potassium iodide:

$$KAuCl_4 + 3KI \rightarrow AuI \downarrow + I_2 + 4KCl$$

Like the silver halides the solubility of the aurous halides also decreases from chloride to the iodide.

24.6.3. Extraction of Gold : Gold being quite inert is found native in some mines. Small amount of gold is also found in the form of sulphide and arsenide. Its extraction procedure involves reaction with sodium cyanide:

$$4Au + 2H_2O + O_2 + 8NaCN \rightarrow 4Na[Au(CN)_2] + 4NaOH$$

Powdered gold ore is treated with sodium cyanide and is agitated with air. The solution of the above aurocyanide is treated with zinc powder when the more electropositive zinc displaces the less electropositive gold:

$$2Na[Au(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Au$$

The crude gold is treated with dilute sulphuric acid to remove any adhered zinc or any accompanying silver. The gold so obtained is again converted to sodium aurocyanide and the solution electrolysed. In this electrolysis plates of pure gold act as cathode while plates made of impure crude gold are used as anodes. As an alternative to electrolysis, impure gold may be mixed with sodium carbonate and charcoal and heated.

Measure of purity of gold: Brightness of gold has been the major attraction behind its being used as a material for ornament. In order to increase the hardness gold is often mixed with copper. Amount of gold in an alloy is expressed as *carat*. Carat is a measure of how many parts of gold are present in 24 parts of an alloy. Thus 10 carat gold means that in the gold alloy out of 24 parts only 10 parts are pure gold i.e. indicates that $(10 \times 100)/24 \simeq 41\%$ gold is present in the alloy. By this measure it follows that real pure gold (100%) has to be 24 carat.

EXERCSIES

1. In what respects the coinage elements are parallel to the alkalies and in what respects do they differ?

2. Present a comparative assessement of the group IB elements.

3. Distinguish between representative and transition elements. Cite some evidence to show that the group IB elements belong to the class of transition elements.

4. Discuss the position of copper, silver and gold in the electrochemical series in relation to the position of the alkalies. Is this in harmony with the reduction potentials of the elements?

5. How do you prepare copper sulphate hydrate? Is it a true vitriol? Will the copper sulphate hydrate form mixed crystals with $FeSO_4.7H_2O$?

6. Write short notes on the following :

(*a*) verdigris (*b*) cupric acetate (*c*) cuprous chloride (*d*) purification of blister copper (*e*) disproportionation (*f*) carat.

7. Give the essential steps involved in the extraction of copper from copper pyrites.

8. Describe the steps and the chemical reactions involved in black and white photography.

9. How would you describe the extraction of silver and gold from their natural sources.

10. Complete the following reactions :

(*a*) $Cu + HNO_3 \rightarrow$
(*b*) $Cu + H_2SO_4 + O_2 \rightarrow$
(*c*) $Na_2S_2O_3 + I_2 \rightarrow$
(*d*) $AgBr + Na_2S_2O_3 \rightarrow$
(*e*) $Na[Ag(CN)_2] + Zn \rightarrow$
(*f*) $Ag + H_2SO_4 \rightarrow$
(*g*) $Au + H_2O + O_2 + NaCN \rightarrow$
(*h*) $AgNO_3 + \text{heat} \rightarrow$

CHAPTER 25

GROUP IIB. ZINC, CADMIUM AND MERCURY

25.1. INTRODUCTION

In the long form periodic table group IIB comes just after group IB. The members of group IB are zinc, cadmium and mercury. The very fundamental difference between group IB and group IIB is that the members of the former group are transition elements while those of the latter are not. Zinc, cadmium and mercury do not show any of the properties like variable valence, coloured compounds and paramagnetism which characterise the transition elements.

25.2. A COMPARATIVE STUDY OF ZINC, CADMIUM AND MERCURY

The ground state outer electronic configuration of these elements is $d^{10}s^2$. Their consistent bivalent state (except the unusual Hg_2^{2+}) has the outer electronic configuration d^{10}. Thus both in the ground atomic state and in the bivalent state they have a filled *d* level. Hence they are to be regarded as representative elements and not as transition elements. Mercury has however a special valence—usually called monovalent mercury—which is bipositive and at the same time dimeric Hg_2^{2+}. There is a mercury—mercury covalent bond, $(Hg\text{-}Hg)^{2+}$, formed by overlap of their *sp* hybridised orbitals. This still leaves two other electrons for valence purpose. Effectively the filled *d* orbitals of mercury still persist. That these three elements cannot be branded as transition elements are evident from the following facts:

1. In all their chemical reactions the filled d^{10} subshell is maintained.
2. Variable valence (with the exception of the very peculiar dimeric Hg_2^{2+} ion) is absent in their chemistry.
3. They do not give coloured compounds except for HgI_2.
4. None of their compounds is known to be paramagnetic. They always produce diamagnetic compounds because they maintain paired spins in all their chemical reactions.

Some of the characteristic chemical properties of these elements are collected in Table 25.1. Some of these properties are not exactly in tune with what we normally observe in a family of well-ordered representative elements. Normally ionisation potentials fall in a group with increasing atomic number. However here in group IIB there is no consistent trend. For reduction potentials, contrary to the trend of a series of good representative elements, the values tend to become less negative and even positive as we move from zinc to mercury. The reduction potentials of zinc and cadmium are negative and hence these two elements can cause liberation of hydrogen from acids. For mercury the reduction potential is positive and hence it fails to displace hydrogen from acids.

Table 25.1. Some Properties of Zinc, Cadmium and Mercury

Element	Atomic Number	Electron Distribution	Ionisation Potential (*ev*)	Electro-negativity	Atomic Radius (A)	M.P (°C)	E^0 (volts)*
Zn	30	$[Ar]3d^{10}4s^2$	9.39 17.96 39.70	1.6	1.33	419	−0.76
Cd	48	$[Kr]4d^{10}5s^2$	8.99 16.90 37.47	1.7	1.49	321	−0.40
Hg	80	$[Xe]4f^{14}5d^{10}$ $6s^2$	10.43 18.75 34.20	1.8	1.50	−38.9	0.79

$*M^{2+} + 2e \rightleftharpoons M$

Chemical Properties: The hydrides of these elements are neither of the ionic type nor of the covalent type. They are not very well defined and in this respect they have some resemblance with the hydrides of the transition elements. There is a difference in the properties of their hydroxides too. Zinc hydroxide is a well known amphoteric hydroxide: it dissolves in acids to give zinc salts while in alkalies we get zincates (ZnO_2^{2-}). Cadmium hydroxide is more basic and less acidic than zinc hydroxide. But mercury hydroxide is a weak base.

The halides of zinc, cadmium are of the ionic type. But mercury chloride is covalent—its aqueous solution is a non-conductor Electrical conductivity of cadmium chloride decreases with increasing concentration due to auto-ionisation: $2CdCl_2 \rightleftharpoons Cd^{2+}[CdCl_4]^{2-}$.

Coordination number of the metals in their complexes is mainly four and the resulting geometry is tetrahedral eg: $[Zn(NH_3)_4]^{2+}$, $[CdCl_4]^{2-}$, $[HgI_4]^{2-}$ etc. In a few limited cases the coordination number is either five or six.

25.3. A COMPARATIVE STUDY OF GROUP IIA AND GROUP IIB

The group IIA elements comprise magnesium, calcium, strontium and barium while group IIB contains zinc, cadmium and mercury. The electron distribution of some of the elements concerned is shown below:

Element	*Atomic number*	*Electron distribution*
Beryllium	4	$[He]2s^2$
Magnesium	12	$[Ne]3s^2$
Barium	56	$[Xe]5s^2$
Zinc	30	$[Ar]3d^{10}4s^2$
Cadmium	48	$[Kr]4d^{10}5s^2$
Mercury	80	$[Xe]4f^{14}5d^{10}6s^2$

The elements of both the subgroups have an s^2 outermost subshell but for the elements of group IIA there is a noble gas core below the s^2 subshell. For the elements of the group IIB there is a d^{10} subshell below the s^2 sublevel.

Both the subgroups show the valence 2. Because of this Mendeleev arranged these elements in two subgroups under the same group II, For the elements of group IIA the ionisation potentials and the reduction potentials continue to decrease with increasing atomic number. But this is not the case with group IIB elements as is evident from Table 25.1. In group IIA beryllium hydroxide alone is amphoteric and all the other hydroxides are only basic. In group IIB zinc hydroxide is distinctly amphoteric. The group IIA elements are very much more ionic in nature than group IIB elements. This follows from the trend of their ionisation potentials.

25.4. A COMPARATIVE STUDY OF GROUP IB AND GROUP IIB

Group IB consists of copper, silver and gold while group IIB has zinc, cadmium and mercury. In the ground atomic states group IB elements have s^1 outermost electronic configuration while the group IIB elements have s^2 arrangement. For both the subgroups there is the filled d^{10} subshell below the outermost s sublevel.

Element	*Atomic number*	*Electron distribution*
Copper	29	[Ar] $3d^{10}4s^1$
Zinc	30	[Ar]$3d^{10}4s^2$

The major difference between these two subgroups is in the extent of their variable valence. The elements of group IB show different oxidation states while those of group IIB show only the bipositive state:

Copper	+3	+2	+1
Silver	+3	+2	+1
Zinc	—	+2	—
Cadmium	—	+2	—

Thus copper, silver and gold are to be classed as transition elements while zinc, cadmium and mercury as representative elements. In keeping with this classification the complexes of copper, silver and gold are coloured while those of zinc, cadmium and mercury are mostly colourless:

Copper sulphate pentahydrate	: blue
Tetrammine copper (II) sulphate	: deep blue
Tetrapyridino silver (II) nitrate	: orange
Silver (I) nitrate	: colourless
Tetrammine zinc (II) sulphate	: colourless
Zinc (II) sulphate heptahydrate	: colourless
Tetraiodo mercury (II)	: colourless

As expected of transition elements compounds of copper, silver and gold show different magnetic behaviour in compounds of different oxidation states:

Copper (I) compounds	$3d^{10}$	: diamagnetic
Copper (II) compounds	$3d^{9}$	: paramagnetic (one unpaired electron)
Silver (I) compounds	$4d^{10}$	: diamagnetic
Silver (II) compounds	$4d^{9}$	: paramagnetic (one unpaired electron)
Zinc (II) compounds	$3d^{10}$	: diamagnetic
Cadmium (II) compounds	$4d^{10}$	: diamagnetic
Mercury (II) compounds	$5d^{10}$	: diamagnetic
Mercurous mercury (I) compounds		: $(Hg—Hg)^{2+}$: diamagnetic

The reduction potentials of copper, silver and gold are all positive: +0.52, +0.79 and +1.68 volts respectively. But in group IIB reduction potentials of zinc and cadmium are negative but that of mercury positive: −0.76, −0.40 and +0.79 volts; $M^{2+}+2e \rightleftharpoons M$. Thus zinc and cadmium can liberate hydrogen from acids while none of copper, silver, gold, mercury can. Dissolution of these metals in non-oxidising acids requires the assistance of oxygen. In oxidising acid like nitric acid they are readily oxidised to the ionic states.

ZINC

25.5.1. Some Compounds of Bivalent Zinc: *Zinc Oxide and Hydroxide*: Commonly the oxide is obtained by heating the metal in air or by decomposing the carbonate by heat:

$$Zn + \tfrac{1}{2}O_2 \rightarrow ZnO;\ ZnCO_3 \rightarrow ZnO + CO_2$$

At ordinary temperature the oxide is colourless but yellow in hot condition. The oxide may be reduced by carbon at *red heat*. This reaction is involved in the extraction of zinc from its ore:

$$ZnO + C \rightarrow Zn + CO$$

The oxide is insoluble in water but dissolves in the presence of alkali due to the formation of zincate ion:

$$2KOH + ZnO \rightarrow K_2ZnO_2 + H_2O$$

This oxide reacts with a drop or two of cobalt nitrate on heating on a charcoal block to give the green mixed oxide, $CoZnO_2$, called Rinmann's green. This is a characteristic test of zinc.

It finds use as a white pigment. It is superior to white lead ($2PbCO_3.Pb(OH)_2$) as it does not turn black in presence of the small amount of the H_2S present in air. But its covering power is inferior to that of white lead. Zinc oxide is also used for polishing porcelain surfaces.

Careful addition of alkali (avoiding excess) to a zinc solution precipitates

$Zn(OH)_2$. On adding more of the alkali the hydroxide dissolves. The hydroxide dissolves also in acids:

$$ZnCl_2 + 2KOH \rightarrow Zn(OH)_2 + 2KCl$$

$$Zn(OH)_2 + 2KOH \rightarrow K_2ZnO_2 + 2H_2O$$

$$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O$$

Potassium zincate can be crystallised in presence of KOH but the salt undergoes hydrolysis in pure water (free from alkali):

$$K_2ZnO_2 + 2H_2O \rightarrow 2KOH + Zn(OH)_2$$

Zinc Sulphate: This is obtained as the well known vitriol $ZnSO_4.7H_2O$ by the reaction of zinc metal or zinc oxide with dilute sulphuric acid. The resulting solution has to be concentrated and crystallised to get the vitriol. Being a true vitriol it is isomorphous with other vitriols like $FeSO_4.7H_2O$, $MgSO_4.7H_2O$, $CoSO_4.7H_2O$ etc. and can form mixed crystals with these compounds. It can be dehydrated by regulated heating but breaks down into zinc oxide on strong heating:

$$ZnSO_4.7H_2O \xrightarrow{\sim 70°C} ZnSO_4.6H_2O \xrightarrow{\sim 300°C} ZnSO_4$$

$$2ZnSO_4 \xrightarrow{\sim 850°C} 2ZnO + 2SO_2 + O_2$$

The compound is very soluble in water. It is used in the making of the well known white pigment *lithopone* which is a mixture of $BaSO_4$ and ZnS:

$$ZnSO_4 + BaS \rightarrow BaSO_4 + ZnS$$

Lithopone has a good covering power and does not readily turn in an atmosphere contaminated with H_2S. Zinc sulphate solution is also used to arrest deterioration of hide, wood. It is a normal practice to get railway line wooden slippers well soaked in a solution of zinc sulphate.

Zinc Chloride: It is usually prepared by the reaction of zinc metal with excess HCl. The resulting solution is concentrated and the temperature raised to about 230°C. At this point the material is mainly anhydrous $ZnCl_2$. The liquid is poured into airtight containers and allowed to solidify. The compound undergoes ready hydrolysis in water free from acids:

$$ZnCl_2 + H_2O \rightarrow Zn(OH)Cl + HCl$$

It is extremely hygroscopic and is sometimes used as an effective desiccant. It is also used to soak railroad wooden slippers in order to arrest deterioration of the wood.

Zinc Sulphide: On the passage of H_2S through an ammoniacal solution of a zinc salt a colourless precipitate of ZnS is obtained:

$$ZnSO_4 + H_2S + 2NH_4OH \rightarrow ZnS + (NH_4)_2SO_4 + 2H_2O$$

The solubility product of ZnS is $\sim 10^{-23}$ whereas that of HgS is $\sim 10^{-52}$. The concentration of sulphide ion in acidic medium is not sufficient enough to exceed the solubility product of ZnS. In the presence of a trace of CuS or MnS zinc sulphide becomes fluorescent. Because of this property of emitting rays even in the dark

Rutherford had used ZnS screen for the counting of alpha particles in a dark room. When alpha, beta or other powerful radiations heat ZnS it is raised to higher energy level. Some of the excited electrons return to the ground state after some time, thereby emitting rays or giving scintillations in a dark room. This property is made use of in reading watch dials at night. Very minute quantity (about one in ten million) of radium salt is mixed with ZnS and the watch dial painted with this sensitised ZnS. The alpha rays strike the fluorescent ZnS and cause the scintillations and thus allow us to read the dial.

25.5.2. Extraction of Zinc: Zinc occurs in nature primarily in two forms: (*a*) zinc blende, ZnS and (*b*) calomine, $ZnCO_3$.

Extraction of zinc from zinc ores is parallel to the extraction of other metals from their sulphide ores. In the case of zinc there is a special advantage in that the metal being comparatively low boiling (907°C) it can be distilled out directly from the reduction reactions.

The most important source of zinc is zinc blende. The ore, as is usual, is admixed with many other undesirable impurities. So the first step involves concentration of the ore. Concentration is achieved via froth floatation process. The powdered ore is mixed with pine oil and water and the suspension agitated with air-blowing. This gives rise to enough frothing which carries along the zinc blende leaving behind much of the undesired impurities. The froth is removed and the concentrated ore is collected.

The enriched zinc blende is now roasted in a stream regulated of air. Excess air is to be avoided so as to prevent formation of the sulphate, which is difficult to reduce:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \quad ; \quad (ZnS + 2O_2 \rightarrow ZnSO_4)$$

The SO_2 obtained as a by product is used in the manufacture of H_2SO_4.

The zinc oxide is now mixed with carbon and heated in retorts (furnace) made of heat resistant refractory bricks. Usually these bricks are made of very high melting silicon carbide (SiC) (Fig. 25.1). The furnace is usually rectangular and has an inlet near the top for the mixture of ZnO and carbon. There is another side tube below the charge inlet for allowing the distilled zinc to pass over. The zinc vapour moves into a cooling chamber where it liquefies and is then drawn out. The reaction furnace is placed inside a big chamber which is provided with several inlets and outlets for the fuel gas. The fuel gas is producer gas ($CO+N_2$) plus air. The charge inside the furnace is also heated with producer gas and air. The temperature inside the furnace is around 1200-1400°C. The ash is taken out through the bottom of the furnace. The outlet tube for zinc vapour near the top of the furnace is generally made of iron which acts as a condenser. The major reaction is:

$$ZnO + C \rightarrow Zn + CO$$

Purification of Zinc: The zinc obtained by the above procedure is quite impure. This crude product contains besides zinc, also lead, cadmium, silicon, carbon, arsenic and some unconverted zinc oxide. The impure zinc is kept in fused state in some retort so as to allow the heavier metals like lead and cadmium to settle at the bottom. The zinc is removed from the upper layer and is distilled several times under reduced pressure to get real pure zinc.

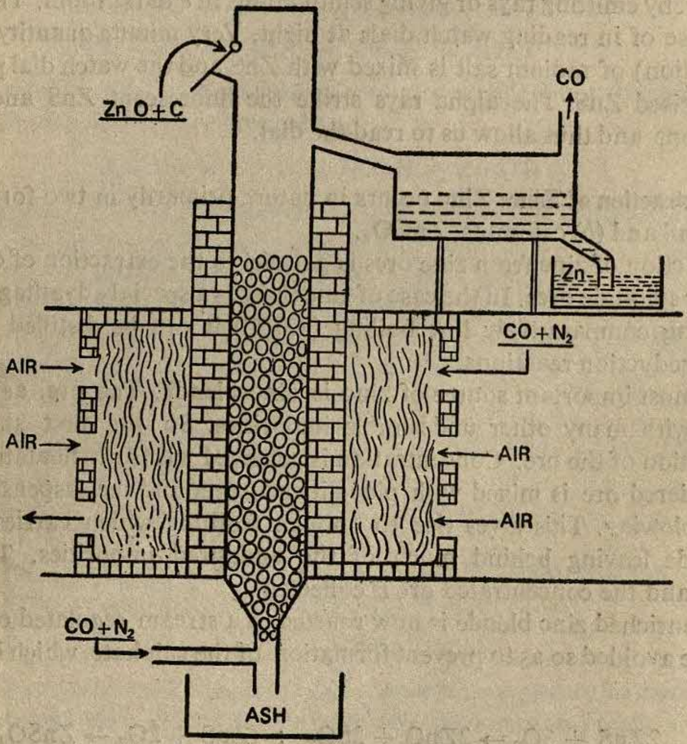


Fig. 25.1. Extraction of zinc from zinc oxide

Purification of crude zinc is also achieved through electrolysis instead of repeated distillation. The process is parallel to what we have seen for copper or silver. Impure zinc plates serve as anodes while pure zinc plates act as cathode. Zinc sulphate solution is used as the electrolyte. Sometimes pure aluminium plates are also used as cathodes. On the passage of current zinc dissolves out into the solution as zinc ions from the anode plates. These bipositive zinc ions migrate to the cathode and are reduced and deposited on the cathode as very pure zinc:

at the anode : $Zn \rightarrow Zn^{2+} + 2e$

at the cathode: $Zn^{2+} + 2e \rightarrow Zn$

Properties of zinc: This is a white metal with a bluish tinge. Its melting and boiling points are 419° and 907°C respectively. It is a good conductor of heat and electricity. It reacts on heating with oxygen, chlorine and sulphur to give ZnO, $ZnCl_2$ and ZnS respectively. It reacts with steam at red heat to give hydrogen:

$$Zn + H_2O \rightarrow ZnO + H_2$$

Although zinc has a good negative reduction potential pure zinc does not readily react with acids to evolve hydrogen. The combination of two hydrogen atoms ($H+H \rightarrow H_2$) to give molecular hydrogen on the surface of pure zinc is real slow. However if the zinc is contaminated with impurities like copper then the formation of H_2 molecules takes place readily on the surface of copper or other impurities. Thus impure zinc reacts faster with acids.

Reactions of zinc with nitric acid are dictated by the concentration of the acid. With concentrated HNO_3 we find NO_2 while with dilute HNO_3, NO is liberated:

$$Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O \text{ (conc. } HNO_3)$$
$$3Zn + 8HNO_3 \rightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O \text{ (dil. } HNO_3)$$

With dilute H_2SO_4 there is evolution of hydrogen whereas with concentrated H_2SO_4 sulphur and H_2S are formed. If the sulphuric acid is very concentrated only SO_2 is given out:

$$Zn + H_2SO_4 \text{ (dilute)} \rightarrow ZnSO_4 + H_2$$
$$4Zn + 5H_2SO_4 \text{ (hot/conc.)} \rightarrow 4ZnSO_4 + H_2S + 4H_2O$$
$$3Zn + 4H_2SO_4 \text{ (hot/conc.)} \rightarrow 3ZnSO_4 + S + 4H_2O$$
$$Zn + 2H_2SO_4 \text{ (very conc.)} \rightarrow ZnSO_4 + SO_2 + 2H_2O$$

Hot and concentrated alkali reacts with metallic zinc to form zincate with evolution of hydrogen:

$$Zn + 2KOH \rightarrow K_2ZnO_2 + H_2$$

Uses: Several alloys of zinc are well known:

Brass: Cu, 60-80%; Zn, 40-20%; used in utensils, cartridge cases etc.

German silver: Cu, 25-50%; Zn, 25-35%; Ni, 10-35%; used in utensils, ornaments etc.

Die-casting alloys: These are made from zinc, copper, tin, aluminium and nickel. These alloys are used in making moulds for metals.

Another important use of zinc is in *galvanising*. To put an end to rusting of iron articles these are covered with a protective layer of zinc—this is achieved by immersing the cleansed iron article like buckets, into molten zinc. This process of covering an article with a layer of zinc is known as galvanising. Another way of having a protective coating of zinc is to take the cleansed article and heat it to a temperature of about 400°C with zinc in a revolving drum. This second process is called *sheradising*.

Coating of zinc may also be given via electrolysis. The cleansed object is made the cathode in an electrolytic cell. Pure zinc is used as anode while a solution of zinc sulphate is taken as the electrolyte. Pure zinc dissolves out at the anode as zinc (II) ions. These ions migrate to the cathode and are deposited on the cathode object.

CADMIUM

25.6.1. Some Compounds of Bivalent Cadmium: *Cadmium oxide and Hydroxide*: The oxide can be obtained by a variety of methods; (a) by heating the metal in air (b) by heating the hydroxide, carbonate or even the nitrate. Depending on the mode of preparation its colour varies from green to brown. A white precipitate of $Cd(OH)_2$ is obtained on the addition of an alkali solution to a solution of a cadmium salt. Cadmium hydroxide is more basic than zinc hydroxide. Therefore it does not dissolve in excess of alkali *i.e.* no cadmiate of the type $[CdO_2]^{2-}$ is formed. It is however readily soluble in acids to give cadmium salts. Cadmium hydroxide reacts with excess ammonia to form the complex $[Cd(NH_3)_4]^{2+}$. Cadmium hydroxide reacts slowly with CO_2 of the air to form $CdCO_3$.

Cadmium Chloride: The chloride is obtained as a pentahydrate after concentrating a solution of cadmium hydroxide or carbonate in HCl acid. The anhydrous $CdCl_2$ may be obtained by heating the pentahydrate in an atmosphere of HCl gas. In the absence of HCl gas heating gives a basic chloride:

$$CdCl_2.5H_2O \rightarrow Cd(OH)Cl + HCl + 4H_2O$$

Measurements on the molecular conductivity shows that with increasing concentration of the chloride conductivity falls. This has been attributed to *autocomplex formation:*

$$2CdCl_2 \rightarrow Cd^{2+} [CdCl_4]^{2-}$$

Cadmium Sulphate: This is prepared by dissolving the hydroxide or the carbonate in dilute H_2SO_4 followed by concentration. Its hydrate has a peculiar formula $CdSO_4.8/3\ H_2O$. It combines with monovalent metal sulphates to give double sulphates of the schonite series: $K_2SO_4.CdSO_4.6H_2O$.

Cadmium Nitrate: Cadmium hydroxide or the carbonate is dissolved in dilute HNO_3 and the solution concentrated to get crystals of the tetrahydrate: $Cd(NO_3)_2.4H_2O$. It is highly hygroscopic.

25.6.2. Extraction of Cadmium : In fact there is no separate ore for the extraction of cadmium. The metal is found in nature alongwith all ores of zinc. For every 200 parts of zinc there is present at least 1 part of cadmium. Thus impure zinc metal contains some cadmium in all cases. The boiling points of the two metals do vary: Zn, 907°C; Cd, 767°C. This difference in the boiling points may be utilised to separate the two elements by repeated distillations.

There is some difference in the standard reduction potentials of the two elements:

$$Zn^{2+} + 2e \rightleftharpoons Zn; E^0 = -0.76 \text{ volts}$$

$$Cd^{2+} + 2e \rightleftharpoons Cd; E^0 = -0.40 \text{ volts}$$

Thus the reducing ability of zinc metal is greater than that of cadmium. Therefore on agitating a cadmium solution with zinc metal there will be precipitation of cadmium metal from solution while zinc metal will pass into solution:

$$Cd^{2+} + Zn \rightarrow Cd \downarrow + Zn^{2+}$$

Properties: The melting and boiling points of cadmium metal are 321°C and 767°C respectively. This is almost white looking in colour. It reacts like zinc although the reactions are less vigorous. With dilute acids it liberates hydrogen. With halogens it produces the appropriate halides.

Uses: Coating of cadmium saves iron or similar articles from rusting or deterioration. An alloy made of Cd, 99%, Ni, 1% or Cd, 98.7%, Ag. 0.7% Cu, 0.6% is used in making engine parts of aeroplanes. Cadmium rods are used in atomic reactors for absorbing excess neutrons,

MERCURY

25.7.1. Some Peculiarities of Mercury : 1. Of all the metals in the periodic table the first ionisation potential of mercury is the highest: 10.43 *ev*. This indicates the inertness of this metal. In keeping with this character we find that its reduction potential is positive: +0.79 volts.

2. Of all the metals in the periodic table mercury is the most volatile: melting point:—38.5°C and boiling point: 357°C.

3. Mercury possesses the special property of dissolving many metals. These special alloys of mercury are known as *amalgams*: Hg_2K, Hg_2Na etc. These amalgams serve as excellent reducing agents in many synthetic work in the laboratory.

4. Mercury is known in two oxidation states: the bivalent Hg^{2+} state and the dimeric bipositive Hg_2^{2+} state, commonly known as the mercurous state. That the mercurous state is not Hg^+ but Hg_2^{2+} is established through a variety of studies:

(a) The variation of molecular conductivity of mercurous nitrate ($Hg_2(NO_3)_2$) in aqueous medium with dilution is comparable to that found for lead nitrate ($Pb(NO_3)_2$). Thus it is inferred that the mercurous ion must also be bipositive i.e. Hg_2^{2+}.

(b) The Hg-Hg distance in several mercurous compounds has been found to be in the range 2.5A. The atomic radius of mercury (Table 25.1) is only 1.5A. Thus it is evident that in the mercurous ion there must exist a Hg-Hg bond as the distance is shorter than the sum of the two single bond radii.

(c) The atomic number of mercury is 80 i.e. the atom has a total of 80 electrons. If the mercurous ion were monomeric monopositive then there would have been one electron less i.e. 79 electrons in the monopositive ion. This would lead to paramagnetism of mercurous compounds. But in reality mercurous compounds are all diamagnetic i.e they have all paired spins. This can be explained on the assumption that the mercurous ion is dimeric and bipositive leading to even number of electrons.

25.7.2. Some Compounds of Bivalent Mercury : *Mercuric Oxide :* This oxide HgO, can be obtained by a variety of methods: (a) by heating mercury in air at about 350°C when red coloured HgO is produced (b) by thermal decomposition of mercuric nitrate $Hg(NO_3)_2$ (c) by the addition of alkali to some mercuric salt solution when yellow coloured HgO is precipitated. The difference in the colour of HgO preparations has been attributed to a difference in the particle size, On strong heating HgO breaks down into mercury and oxygen:

$$2HgO \rightarrow 2Hg + O_2$$

This reaction has gone down the memory lane because Lavoisier proved through heating of mercury in air and reheating of HgO that air is composed of almost one-fifth of oxygen and four-fifths of an inert gas, now called nitrogen.

Mercuric Chloride (*Corrosive Sublimate*): Mercury can be oxidised by heating in chlorine to give $HgCl_2$ which is purified by sublimation. On heating a mixture of $HgSO_4$ and NaCl, $HgCl_2$ is formed which sublimes:

$$HgSO_4 + 2NaCl \rightarrow Na_2SO_4 + HgCl_2$$

Mercuric chloride is soluble in water. In the presence of added chloride ion its solubility increases because of the formation of the tetrahedral $HgCl_4^{2-}$. It is reduced by $SnCl_2$ first to the insoluble mercurous chloride Hg_2Cl_2 (colourless) and then to the black mercury:

$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2\downarrow + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg\downarrow + SnCl_4$$

It reacts very rapidly with proteins and hence is very poisonous. Its antidote is the white albumin of fresh raw egg. Therefore on swallowing accidentally any little amount of $HgCl_2$ the white albumin should be given as a first aid. The albumin adsorbs $HgCl_2$ and makes it unavailable to the proteins.

Potassium iodide reacts with mercuric chloride to precipitate red HgI_2 which dissolves in excess KI to form the colourless soluble complex $K_2[HgI_4]$:

$$HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl \ ; \ HgI_2 + 2KI \rightarrow K_2[HgI_4]$$

On making the solution of K_2HgI_4 alkaline with NaOH or KOH we get Nessler's reagent which is used in the detection of ammonium ion (Chapter 28).

Mercuric chloride reacts with ammonia to give a white precipitate of amidomercuric chloride ($NH_2—Hg—Cl$). It cannot be fused; hence it is also called infusible white precipitate.

Mercuric Nitrate: This is obtained as a dihydrate, $Hg(NO_3)_2.2H_2O$, on concentrating the solution obtained by dissolving mercury in nitric acid. Solution of mercuric nitrate remains stable in the presence of little HNO_3. In neutral water there is a precipitate of basic mercuric nitrate:

$$3Hg + 8HNO_3 \rightarrow 3Hg(NO_3)_2 + 2NO + 4H_2O$$

$$4Hg(NO_3)_2 + 2H_2O \rightarrow 2Hg(NO_3)_2.2HgO + 4HNO_3$$

Mercuric Sulphide: This compound is obtained in two forms: (a) black amorphous HgS and (b) red crystalline HgS. The black form is usually obtained on the passage of H_2S through a solution of a mercuric salt in acid medium. The solubility product is very low $\sim 10^{-52}$. As H_2S is bubbled through a mercuric solution the colour of the precipitate changes from whitish to yellowish brown and then to black. The intermediate products are due to mixed compounds like $HgCl_2.2HgS$ etc (Chapter 28):

$$HgCl_2 + H_2S \rightarrow 2HCl + HgS$$

On heating black HgS sublimes and gives beautiful red coloured HgS, known as vermillion. This red variety is a valuable pigment. HgS is usually soluble in aqua regia. On strong heating HgS decomposes to mercury and sulphur. On heating in oxygen we get mercury and sulphur dioxide:

$$HgS + O_2 \rightarrow Hg + SO_2$$

Although vermillion is a very good pigment it is very costly. It is therefore often substituted by red lead, Pb_3O_4.

Mercuric Iodide: On treating a mercuric chloride solution with two molar proportions of KI a beautiful red precipitate of HgI_2 is obtained. Excess KI dissolves it out to the soluble complex K_2HgI_4:

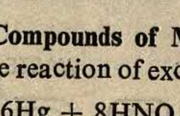
$$HgCl_2 + 2KI \rightarrow \underset{\text{(red)}}{HgI_2} + 2KCl \;;\; HgI_2 + 2KI \rightarrow \underset{\text{(colourless)}}{K_2[HgI_4]}$$

Reactions between mercuric salts and ammonia: The following equilibria exist between mercuric chloride and ammonia:

$$HgCl_2 + 2NH_3 \rightleftharpoons Hg(NH_3)_2Cl_2\downarrow$$

$$HgCl_2 + 2NH_3 \rightleftharpoons Hg(NH_2)Cl\downarrow + NH_4^+ + Cl^-$$

The equilibrium of the second reaction shows that in the presence of added common NH_4^+ ion the precipitate of $Hg(NH_2)Cl$ is less likely to appear as the reaction will be forced to proceed from the right to the left. In fact in the presence of NH_4Cl addition of ammonia precipitates $Hg(NH_3)_2Cl_2$—a tetrahedral complex of mercury (II). On the contrary if ammonia alone is added to mercuric chloride the white infusible precipitate, $Hg(NH_2)Cl$, (amido chloro mercury (II)) is obtained.



dichloro diammine mercury (II)
(fusible white precipitate)
(tetrahedral)

$$H_2N - Hg - Cl$$

amido chloro mercury (II)
(infusible white precipitate)
(linear)

25.7.3. Some Compounds of Mercurous Mercury : *Mercurous Nitrate :* This is prepared by the reaction of excess mercury with hot dilute HNO_3:

$$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$

The compound is hydrolysed by water:

$$Hg_2(NO_3)_2 + H_2O \rightarrow Hg_2(OH)(NO_3) + HNO_3$$

It reacts with chloride ion to give a colourless silky precipitate of mercurous chloride:

$$Hg_2(NO_3)_2 + 2HCl \rightarrow Hg_2Cl_2\downarrow + 2HNO_3$$

On heating the compound decomposes as:

$$Hg_2(NO_3)_2 \rightarrow 2HgO + 2NO_2$$

Mercurous Chloride: This compound, Hg_2Cl_2, is also known as *calomel*. This can be obtained by double decomposition between mercurous nitrate and HCl. Alternatively this can be prepared by reducing mercuric chloride with mercury. A mixture of mercury and $HgCl_2$ is sublimed when Hg_2Cl_2 condenses. This Hg_2Cl_2 contains some $HgCl_2$ as impurity. The crude mixture is stirred with water to remove the soluble $HgCl_2$. In the laboratory this can be prepared by heating a mixture of excess mercury and less HNO_3 (9:8) when a solution of the mercurous nitrate is formed. This solution is treated with NaCl and little HCl to get the precipitate of Hg_2Cl_2:

$$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$
$$Hg_2(NO_3)_2 + 2NaCl \rightarrow Hg_2Cl_2 + 2NaNO_3$$

On strong heating the compound decomposes:

$$Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2$$

Reaction of Hg_2Cl_2 *with ammonia:* The reaction of ammonia and Hg_2Cl_2 first produces colourless $H_2N-Hg-Hg-Cl$ which decomposes to metallic mercury, chloroamido mercury (II) and NH_4Cl. The product finally looks black due to mercury:

$$Hg_2Cl_2 + 2NH_3 \rightarrow H_2N-Hg-Hg-Cl + NH_4Cl$$
$$H_2N-Hg-Hg-Cl \rightarrow Hg + H_2N-Hg-Cl$$

25.7.4. Extraction of Mercury : The major source of mercury is cinnabar (HgS). This ore is found in only a few places in the world: at Almadel in Spain, at California in U.S.A. and at Tuscany in Italy. The chemistry of the extraction process

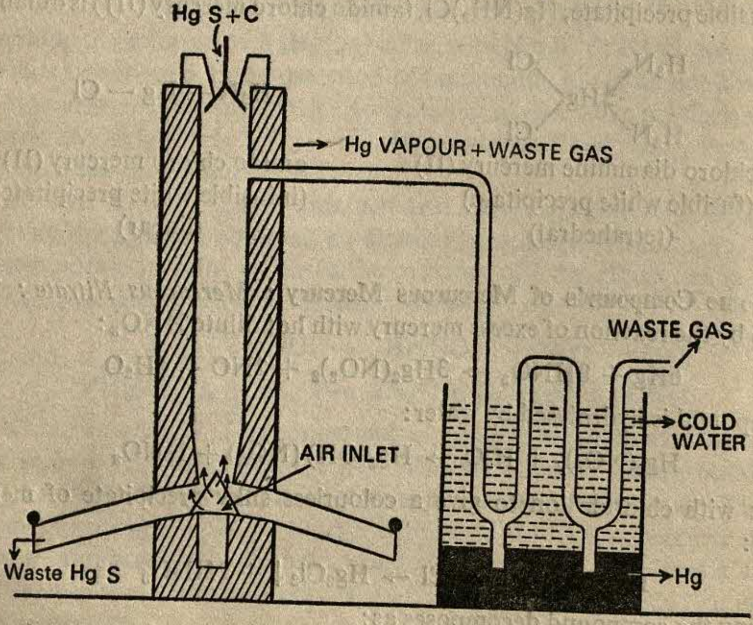


Fig. 25.2. Extraction of mercury from cinnabar

is simple enough. On heating HgS in a current of air SO_2 is evolved and mercury distills off. The mercury and SO_2 vapour are led through condensers where mercury collects in the liquid form and SO_2 passes through:

$$HgS + O_2 \rightarrow Hg + SO_2$$

Small version of blast furnaces is used. Through the top cup and cone arrangement (Fig. 25.2) the charge—a mixture of HgS and charcoal—is pushed inside the blast furnace. Through the lower portion of the furnace hot blast of air is introduced. In the presence of charcoal several reactions occur. Finally mercury vapour and SO_2 and CO/CO_2 travel upwards and pass through the series of condensers. Mercury condenses to the liquid form and is collected under water:

$$2HgS + 3O_2 \rightarrow 2HgO + 2SO_2 \text{ ; } HgO + C \rightarrow Hg + CO$$
$$2HgO \rightarrow 2Hg + O_2 \text{ ; } CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

Purification of Mercury: The mercury as obtained above carries some metals as impurities. These metals are lead, zinc, tin and bismuth. These impure metals are all more electropositive than mercury and hence are more easily oxidised than mercury. Therefore in the laboratory the crude mercury is allowed to drop through a long column of a solution of 5 % HNO_3 and little $Hg_2(NO_3)_2$ (Fig. 25.3). The column is usually 70-80 cm long and is provided with a bent capillary tube to regulate slow flow-out of the mercury thus allowing more time for purification. The impurities are readily oxidised to their ions by the HNO_3 and stay in the solution as nitrates, Mercurous nitrate also helps in the conversion of the other impurities to the nitrate state:

$$Pb + Hg_2(NO_3)_2 \rightarrow 2Hg + Pb(NO_3)_2$$

Properties: Mercury is a silvery liquid metal. It is very heavy (density, 13.6 at 0°C). Its boiling point is 357°C. In the gaseous state it is monomeric. One of the outstanding properties of the metal is its ability to dissolve other metals to give what we call *amalgams*. The alkali metal amalgams are very useful as reducing agents in various syntheses in the laboratory. On heating with oxygen, sulphur etc. it gives oxide, sulphide etc. With the halogens mercuric compounds are formed readily:

$$2Hg + O_2 \rightarrow 2HgO \text{ ; } Hg + S \rightarrow HgS$$
$$Hg + Cl_2 \rightarrow HgCl_2 \text{ ; } Hg + I_2 \rightarrow HgI_2$$

It reacts with hot concentrated H_2SO_4 to give $HgSO_4$:

$$Hg + 2H_2SO_4 \rightarrow HgSO_4 + SO_2 + 2H_2O$$

Uses: Mercury is extensively used in thermometers, barometers, mercury lamps. In many industrial processes mercury is used as cathode. Amalgams are also in demand. Mercuric oxide, chloride and mercurous chloride are used in medicine,

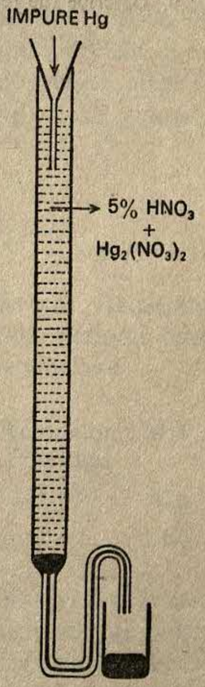


Fig. 25.3. Purification of mercury

EXERCISES

1. Among metals mercury has many peculiarities. Outline these peculiarities and their implications in its chemistry.

2. Present a comparative account of zinc, cadmium and mercury.

3. Compare and contrast groups IIA and IIB.

4. What are the fundamental differences in the chemistries of copper, silver and gold on the one hand and zinc, cadmium and mercury on the other?

5. What evidences show that mercurous mercury is really dimeric and dipositive and not monomeric and monopositive.

6. Give the preparation and properties of the following :

(*a*) mercurous chloride (*b*) mercuric nitrate (*c*) dichlorodiammine mercury (II) (*d*) Nessler's reagent (*e*) amalgams

7. Give the essentials of extraction of zinc and cadmium and their purification.

8. Complete the following reactions :

(*a*) $ZnCl_2$ and excess KOH →

(*b*) $ZnSO_4 + BaS \rightarrow$

(*c*) $Zn + HNO_3 \rightarrow$

(*d*) $HgCl_2 +$ excess $SnCl_2 \rightarrow$

(*e*) $HgCl_2 + 2NH_3 \rightarrow$

(*f*) $Hg_2Cl_2 + 2NH_3 \rightarrow$

9. Describe the reactions of mercury with H_2SO_4 and HNO_3.

CHAPTER 26

RADIUM, THORIUM AND URANIUM : THREE RADIOACTIVE ELEMENTS

26.1. INTRODUCTION

Three important radioactive elements, namely radium, thorium and uranium, form the subject matter of discussion of this Chapter. We have already looked into the properties of radioactive elements in Chapter 2. Radioactive elements usually emit three kinds of radiation: alpha rays, beta rays and gamma rays. Alpha emission reduces the atomic number and mass number of the product element by 2 and 4 units respectively. Beta rays, being electrons, lead to an increase in the atomic number of the product element by one unit but do not lead to any change in the mass number. Gamma rays are high energy radiations and often accompany alpha and beta emission. The three elements under discussion in this Chapter are mainly alpha emitters. Radium is a representative element and belongs to the second group of the periodic table. Thorium and uranium are members of the second inner transition series i.e. the family of the actinides. (Chapters 1 and 3).

26.2. CHEMISTRY OF RADIUM

26.2.1. General Observations: Radium is a representative element. Its electron configuration allows us to place the element in group IIA of the periodic table. Its electron configuration and some physical properties are shown below:

Element	Atomic Number	Electron Distribution	Ionisation Potential	M^{2+} Radius	Reduction Potential	M.P.
Radium	88	$[Rn]7s^2$	5.27 10.14 *ev*	1.50A	−2.92 volts	960 (°C)

The electron distribution clearly shows that once the element loses its two 7*s* electrons it can move on to the stable electronic configuration of the noble gas radon. In fact radium does behave as a bivalent element all through and is rightly placed in the group II A of the periodic table. In keeping with the behaviour of the representative elements its ionisation potential and electronegativity are the lowest in te series: magnesium, calcium, strontium, barium and radium. Thus in this group radium is the most electropositive element.

Radium chloride forms a dihydrate $RaCl_2.2H_2O$. This is isomorphous with the corresponding barium salt, $BaCl_2.2H_2O$. Radium sulphate is quite insoluble and again is isomorphous with the barium analogue $BaSO_4$. The compounds of radium are all ionic in nature and exhibit all properties expected of ionic compounds. Thus fused anhydrous $RaCl_2$ is a conductor of electric current. In fact Marie Curie utilised this property of fused $RaCl_2$ in the isolation of radium metal.

26.2.2. Preparation of Radium from Pitchblende: Pitchblende is essentially U_3O_8. In nature it is mixed up with compounds of thorium, lead, vanadium etc. Pitchblende contains but a minute amount of radium. The ore is treated with H_2SO_4. The solution so obtained contains the very little radium as radium sulphate. Although $RaSO_4$ is essentially insoluble it is not precipitated out because of its very small amount. The solution is treated with $BaCl_2$. The precipitated $BaSO_4$ carries down with it the small amount of $RaSO_4$. The mixture of $BaSO_4$ and $RaSO_4$ is mixed with Na_2CO_3 and then fused. The mass is then treated with HCl when $BaCl_2$ and $RaCl_2$ pass on to the solution phase. This solution is fractionally crystallised for a number of times. The more soluble $BaCl_2$ is retained in the mother liquor while $RaCl_2$ crystallises out. The radium chloride dihydrate is then dehydrated and fused. The fused radium chloride is then electrolysed with mercury cathode. At the cathode radium is deposited on mercury and forms an amalgam. On careful of the amalgam distillation mercury is removed and metallic radium is recovered.

Radium is a colourless metal. It reacts vigorously with water to give off hydrogen and to form $Ra(OH)_2$. The metal thus resembles the alkaline earths.

26.2.3. Radioactivity of Radium : The element has as many as four isotopes : radium-228, radium-226, radium-224 and radium-223. Of these radium-228 alone is a beta emitter and the rest are alpha emitters. Properties of these isotopes are given below:

Isotope	Alpha/Beta Emission	Disintegration	Half-life
Radium-228	Beta	${}^{228}_{88}Ra \rightarrow {}^{228}_{89}Ac + {}^{0}_{-1}e$	6.7 years
Radium-226	Alpha	${}^{226}_{88}Ra \rightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$	1590 years
Radium-224	Alpha	${}^{224}_{88}Ra \rightarrow {}^{220}_{86}Rn + {}^{4}_{2}He$	3.64 days
Radium-223	Alpha	${}^{223}_{88}Ra \rightarrow {}^{219}_{86}Rn + {}^{4}_{2}He$	162 days

26.2.4. Uses of Radium : Alpha radiations from radium are used in treatment of cancer and similar other diseases. Very minute amount of radium salts is used along with ZnS, CaS or lithopone ($ZnS + BaSO_4$) in dials of watches. These paints are fluorescent. When alpha rays from radium strike these compounds the outer electrons of these elements (Zn. Ca, Ba) are excited to higher energy levels. While reversing back to the original level the extra energy is released in the form of light, which makes it easy to read watch dials even in the dark.

26.3. THORIUM

26.3.1. Chemistry of Thorium : Thorium is a member of the second series of the inner transition elements (Chapter 1). Its electron distribution and some relevant properties are given below:

Element	Atomic Number	Electron Distribution	Ionisation Potential	M^{4+} radius	M.P. (°C)
Thorium	90	$[Rn]6d^27s^2$	6.11, 11.4(*ev*)	0.99A	1750

The electron distribution, at first sight, might give us an idea that the element is likely to give more than one valence because the electrons are distributed over two quantum levels. However as the principal quantum number continues to increase the energy gaps between the levels continue to decrease. It is primarily the explanation why we always find one valence, namely quadrivalence, in thorium. No other valence is shown by this element. The size of the Th^{4+} ion is pretty big and at the same time the charge is also high enough. Thus we expect, following Fajans, that there should be both ionic as well as covalent compounds in thorium chemistry.

Thorium Dioxide: Thorium hydroxide, $Th(OH)_4$, appears as a jelly like compound on the addition of NaOH to a soluble thorium compound. Characteristic of strong bases the hydroxide absorbs CO_2 from the air. On heating the hydroxide changes over to the dioxide ThO_2.

Thorium Halides: All the four halides are known. The common expected procedure is to carry out the reaction between thorium metal and the dry halogens. Alternatively the dioxide may be heated with the halogens in the presence of carbon. All the halides show ionic properties. These have moderately high melting points and conduct electricity in the fused state.

Complexes: Thorium (IV) is known to give complexes with fluoride ion, oxalate ion, ethylenediamine tetraacetic acid etc. These complexes are either six- or eight- coordinated: $M_2[ThF_6]$; M_4 $[Th(Ox)_4]$ (Ox^{2-} = oxalate ion); $[Th(EDTA)(H_2O)_2]$ (EDTA H_4 = ethylenediamine tetraacetic acid). Note that eight coordination is prominent because of the large size of the quadrivalent thorium ion.

26.3.2. Preparation of thorium : Commercially monazite sand is the most important ore of thorium. Monazite is found in abundant quantity in the sandy coasts of Kerala (India) and Brazil. Monazite is primarily a complex phosphate of the lanthanides but contains also small amounts of thorium and uranium.

Monazite sand is first concentrated by shaking under running water. Thereafter it is worked up with hot H_2SO_4 and then filtered. The lanthanides alongwith thorium and uranium pass onto the solution phase. The solution is next treated with KIO_3 when thorium iodate $Th(IO_3)_4$ is precipitated. This precipitate is slightly contaminated by uranium iodate. But the lanthanides are retained in solution. The precipitate is ignited when ThO_2 and U_3O_8 are obtained. The oxide mixture is converted to $Th(NO_3)_4$ and $UO_2(NO_3)_2$. An acid solution (6M HNO_3) (of these nitrates) is shaken with some suitable immiscible organic solvent like tributylphosphate and the organic layer is separated and stripped with water. Such solvent extraction leaves thorium in the aqueous phase and the uranium in the organic solvent. The pure thorium nitrate thus obtained gives pure ThO_2 on ignition. This oxide is further reacted with chlorine in the presence of carbon to provide anhydrous $ThCl_4$. This chloride is mixed with KCl and NaCl and fused. The fused material is then electrolysed using a carbon crucible as anode and a molybdenum rod as the cathode. Pure thorium is deposited at the cathode while chlorine is liberated at the anode.

26.3.3. Radioactivity of Thorium : The element has a number of radioactive isotopes most of which are alpha emitters. A profile of these isotopes is given below:

Isotope	Alpha/Beta Emitter	Radioactive Disintegration	Half-life
Th-232	Alpha	${}^{232}_{90}\mathrm{Th} \rightarrow {}^{228}_{88}\mathrm{Ra} + {}^{4}_{2}\mathrm{He}$	1.4×10^{10} years
Th-228	Alpha	${}^{228}_{90}\mathrm{Th} \rightarrow {}^{224}_{88}\mathrm{Ra} + {}^{4}_{2}\mathrm{He}$	1.9 years
Th-229	Alpha	${}^{229}_{90}\mathrm{Th} \rightarrow {}^{225}_{88}\mathrm{Ra} + {}^{4}_{2}\mathrm{He}$	7.3×10^{3} years
Th-234	Beta	${}^{234}_{90}\mathrm{Th} \rightarrow {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}e$	24.1 days
Th-230	Alpha	${}^{230}_{90}\mathrm{Th} \rightarrow {}^{226}_{88}\mathrm{Ra} + {}^{4}_{2}\mathrm{He}$	8×10^{4} years
Th-227	Alpha	${}^{227}_{90}\mathrm{Th} \rightarrow {}^{223}_{88}\mathrm{Ra} + {}^{4}_{2}\mathrm{He}$	18.4 days

26.3.4. Uses of Thorium : An alloy made of 97% magnesium and 3% thorium finds use in the construction of aeroplanes and missiles. The gas mantles have their incandescent filament made of ThO_2 and 1% CeO_2. However the future major possible use lies in harnessing atomic power from this element. Thorium-232 can absorb a neutron to become thorium-233. This thorium-233 may break up into protactinium-233 which may then break up into uranium-233. This uranium-233 isotope is fissionable i.e. it can take up a neutron and undergo fission releasing energy.

$$\begin{tikzcd}
{}^{232}_{90}\mathrm{Th} + {}^{1}_{0}n \arrow[r] & {}^{233}_{90}\mathrm{Th} \arrow[r] & {}^{233}_{91}\mathrm{Th} + {}^{0}_{-1}e \arrow[d, "{}^{1}_{0}n"'] \\
& \text{energy + nuclear fission} & {}^{233}_{92}\mathrm{U} \arrow[l]
\end{tikzcd}$$

26.4. URANIUM

26.4.1. Chemistry of Uranium : Uranium is a typical member of the actinide series of the second inner transition elements. It is one of the most outstanding radioactive elements of the periodic table and is instrumental in generation of atomic power energy. The relevant data on the element are given below:

Element	Atomic Number	Electron Distribution	M^{4+} ion radius	Melting Point (°C)
Uranium	92	$(Rn)5f^36d^17s^2$	0.93A	1132

While thorium consistently shows quadrivalence uranium exhibits several valences: +6, +5 and +4. Of these hexavalent uranium is the stablest and commonest.

Hexavalent Uranium: As a general rule higher valent oxides are acidic. We find that UO_3 is amphoteric. It reacts with acids to produce salts of the type UO_2Cl_2, $UO_2(NO_3)_2$, UO_2SO_4 etc. It also reacts with bases to produce salts of the type $Na_2U_2O_7$. The usual diuranyl salts have a trans $O = U = O$ linking. The uranyl ion is also known to give a number of complexes with the *trans* $O{=}U{=}O$ intact. Some of the complexes are $[UO_2(acac)_2]$, $[UO_2(oxin)_2]$ oxin H (acacH = acetylacetone; oxin H = 8-hydroxyquinoline). When uranium salts are treated with ammonia $(NH_4)_2U_2O_7$ is precipitated. On ignition this precipitate gives U_3O_8. This yellow oxide may be dissolved in appropriate acids to get the uranyl salts. Uranyl salts are usually obtained with a greenish tinge.

Pentavalent Uranium: This oxidation state of uranium is usually unstable and readily disproportionates into uranium (VI) and uranium (IV):

$$2U(V) \rightarrow U(VI) + U(IV)$$

These are usually made by the oxidation of uranium (IV):

$$2UCl_4 + Cl_2 \xrightarrow{520°C} 2UCl_5$$

Pentavalent uranium has one unpaired electron in the 5*f* subshell. This makes all uranium (V) compounds paramagnetic. UCl_5 is used as a starting material for the syntheses of other uranium (V) compounds:

$$UCl_5 + 5ROH + 5NH_3 \rightarrow U(OR)_5 + 5NH_4Cl$$

Quadrivalent Uranium: The oxide UO_2 is essentially basic in nature. This oxide is obtained on reduction of UO_3 or U_3O_8 by carbon or hydrogen at elevated temperature. The tetrahalides are prepared by (a) the reaction of uranium with halogens or (b) by reacting U_3O_8 with halogens in the presence of carbon. Hexavalent uranium salts can also be reduced by stannous chloride, zinc amalgam:

$$UO_2(CH_3COO)_2 + Zn + 4CH_3COOH \rightarrow Zn\,[U(CH_3COO)_6] + 2H_2O$$

$$UO_2Cl_2 \xrightarrow[HCl]{reduction} UCl_4 \xrightarrow{pyH.Cl} (pyH)_2(UCl_6)$$

Quadrivalent uranium has two unpaired spins in the 5*f* subshell and hence the compounds are expected to be paramagnetic.

26.4.2. Radioactivity of Uranium : All the naturally occurring isotopes of uranium are alpha emitters. Their characteristic properties are assembled below:

Isotope	Alpha/Beta Emitter	Radioactive Disintegration	Half-life
U-238	Alpha	${}^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He$	4.5×10^9 years
U-235	Alpha	${}^{235}_{92}U \rightarrow {}^{231}_{90}Th + {}^{4}_{2}He$	7.1×10^8 years
U-234	Alpha	${}^{234}_{92}U \rightarrow {}^{230}_{90}Th + {}^{4}_{2}He$	2.48×10^5 years
U-233	Alpha	${}^{233}_{92}U \rightarrow {}^{219}_{90}Th + {}^{4}_{2}He$	1.62×10^5 years

26.4.3. Preparation of Uranium : Two important ores of uranium are pitchblende (primarily U_3O_8) and uraninite (primarily UO_2+UO_3). The ores are worked up with HNO_3 when uranium passes into solution as soluble $UO_2(NO_3)_2$. The solution is then shaken with immiscible organic solvents like tributyl phosphate or methyl isobutyl ketone. The uranyl salt is more soluble in the organic solvent than the other constituents. The organic solvent is then separated and shaken with water when the uranyl salt passes back into the aqueous layer. Several such extractions into organic solvent and back again into the aqueous layer gives a reasonably pure form of $UO_2(NO_3)_2$. The salt is then heated to get UO_3. This oxide is heated with chlorine in presence of carbon to get pure UCl_4. This chloride is mixed with pure powdered magnesium and heated when pure uranium metal collects below the layer of fused $MgCl_2$: $UCl_4 + 2Mg \rightarrow U + 2MgCl_2$

26.4.4. Uses of Uranium : We have already seen how uranium-235 can undergo nuclear fission on bombardment with neutrons and can liberate huge energy. This energy has been used both for destructive purposes as well as for harnessing power for mankind. The major peaceful use of the element is in modern atomic reactors for generating electricity (Chapter 2).

EXERCISES

1. Radium-224, thorium-234 and uranium-235 are known to be alpha beta- and alpha emitter respectively. Write down the radioactive transformations and explain.

2. Give an account of the radioactivity of radium, thorium and uranium. Also discuss their major uses.

3. Is their any basic difference between radioactive elements and non-radioactive elements so far as their arrangement in the periodic table is concerned?

4. What properties have allowed us to include radium in the group IIA of the periodic table?

5. Give an account of how uranium-235 liberates huge amount of energy (see Chapter 2).

CHAPTER 27

DETERMINATION OF THE FORMULA OF SOME CHEMICAL COMPOUNDS

27.1. INTRODUCTION

In all chemical studies a knowledge of the formula of the chemical compounds is essential. If the compound is crystalline it is easier to establish its formula. As an example we can take the case of nickel sulphate heptahydrate. We can take a weighed quantity of the compound and precipitate its nickel in ammoniacal medium with the help of dimethylglyoxime. The precipitated bis (dimethylglyoximato) nickel (II) may be filtered, washed, dried at 120°C and weighed. From the knowledge of the weight of the precipitate we can calculate the percentage of nickel present in the original nickel salt (Chapter 29). In another weighed amount of the nickel sulphate the sulphate anion may be precipitated as barium sulphate and the precipitate weighed. From the weight of the $BaSO_4$ precipitate we can calculate the percentage of the sulphate present in the sample. In a third weighed amount we can determine the hydrate water by dehydrating the sample under controlled heating. This will give us the percentage of the water content of the sample. Thus determinations of the percentage of nickel, sulphate and water will reveal the true formula of nickel sulphate heptahydrate.

There are several instances where the compounds exist as liquids and gases. There is no hard and fast rule about how to proceed to determine the molecular formula in such cases. Special methods have to be adopted for special compounds. In this Chapter we describe the determination of molecular formula of eight important gaseous or liquid compounds or mixtures.

27.2. AVOGADRO HYPOTHESIS AND DIATOMICITY OF ELEMENTARY GASES

Avogadro hypothesis states that at a given set of temperature and pressure equal volumes of gases contain equal number of particles i.e. molecules. With the help of this hypothesis it was possible to conclude that gases like chlorine, oxygen, hydrogen are made of diatomic molecules.

We take the case of formation of hydrogen chloride gas from hydrogen and chlorine. Experiments show that two equal volumes of hydrogen and chlorine react with each other to generate hydrogen chloride gas of twice the volume of hydrogen or chlorine. According to Avogadro hypothesis both the original volumes of hydrogen and chlorine contains the same number of molecules. Let us take this number to be x.

Therefore x molecules of hydrogen and x molecules of chlorine combine to produce 2x molecules of hydrogen chloride gas.

Thus 1 molecule of hydrogen combines with 1 molecule of chlorine to give 2 molecules of hydrogen chloride. Therefore for 1 molecule of hydrogen chloride we need $\frac{1}{2}$ molecule of hydrogen and $\frac{1}{2}$ molecule of chlorine. In order to keep Dalton's proposition of indivisibility of atoms intact we have to assume that in 1 molecule of hydrogen chloride we must have a minimum of 1 atom of hydrogen and 1 atom of chlorine. The inevitable conclusion is that 1 atom of hydrogen and 1 atom of chlorine have to come from $\frac{1}{2}$ molecule of hydrogen and $\frac{1}{2}$ molecule of chlorine respectively. This immediately proves that hydrogen and chlorine form diatomic molecules.

That oxygen is also diatomic can be proved from a study of the composition of water. Chemical experiments tell us that:

2 volumes of hydrogen + 1 volume of oxygen → 2 volumes of steam
2x molecules of hydrogen + x molecules of oxygen → 2x molecules of steam
1 ,, ,, + $\frac{1}{2}$,, ,, → 1 ,, ,,

1 molecule of steam must contain at least one atom of oxygen, if we are not to flout Dalton's indivisibility of atoms. Thus 1 atom of oxygen comes from $\frac{1}{2}$ molecule of oxygen i.e. a molecule of oxygen is composed of 2 atoms. Oxygen is thus a diatomic molecule.

27.3. DETERMINATION OF FORUMLA OF WATER

Several chemists have applied several different procedures for determining the formula of water. All these researches have proved beyond doubt that water has the chemical formula H_2O. We discuss below two methods: (1) Hoffman's volumetric procedure and (2) Dumas' gravimetric procedure.

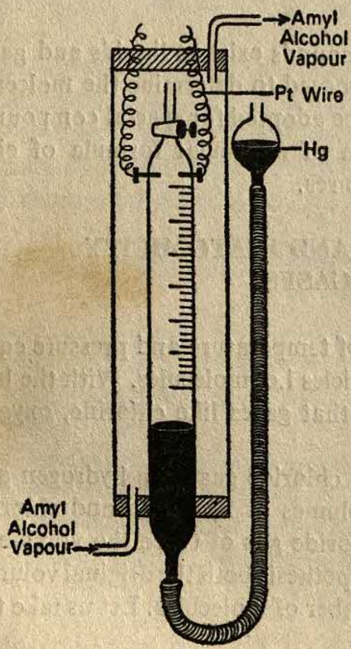


Fig. 27.1. Hoffman's procedure for determination of formula of water

27.3.1. Hoffman's Volumetric Procedure: A stout graduated tube is provided with a stop-cock at one end and the other end is drawn out and connected by a pressure tube to a mercury reservoir. Below the the stop-cock there are two platinum wires sealed into the tube. The platinum wires may be connected to high voltage source so as to pass spark inside the graduated tube. The graduated eudiometer tube is placed inside a glass jacket which is provided with an inlet and outlet for boiling amyl alcohol vapour (B.P. 132°C). This is done to keep the water resulting from sparking of the oxygen—hydrogen mixture above its boiling point.

Hoffman introduced two volumes of pure hydrogen and one volume of pure oxygen into the eudiometer tube. The total volume of the gas mixture was read at the temperature of the amyl alcohol vapour. Thereafter the gas mixture was sparked to form steam at that temperature. After the sparking was over the volume of steam was noted at 132°C. The mercury levels inside the eudiometer tube and in the outer bulb were adjusted to the same volume which gave a measure of the volume of the gas inside the tube at ordinary temperature and pressure. Such experiment showed that out of the combination of two volumes of hydrogen and one volume of oxygen only two volumes of steam were produced. Applying Avogadro hypothesis:

2 volumes of hydrogen + 1 volume of oxygen → 2 volumes of steam
2 molecules of hydrogen + 1 molecule of oxygen → 2 molecules of steam
1 ,, ,, + $\frac{1}{2}$,, ,, → 1 ,, ,,
2 atoms of hydrogen + 1 atom of oxygen → 1 ,, ,,
Thus the formula of steam is H_2O.

We can also arrive at the same formula in a little simplified way also. Since hydrogen and oxygen are diatomic and since two volumes of water are produced we can write: $2H_2 + O_2 \rightarrow 2H_mO_n$

This equation can be balanced only if $m = 2$ and $n = 1$ i.e. water has the formula H_2O.

27.3.2. Dumas' Gravimetric Procedure :Dumas produced water by a very different method: $CuO + H_2 \rightarrow Cu + H_2O$

Dumas used very pure quality cupric oxide and very pure hydrogen for the above reaction. Hydrogen, prepared from zinc and sulphuric acid, was passed through a series of bubblers containing (a) lead nitrate to remove H_2S (b) silver nitrate to remove AsH_3 and PH_3 (c) potassium hydroxide to remove acidic oxides like CO_2, SO_2, NO_2 etc (d) phosphorus pentoxide to remove any moisture. So very pure hydrogen was then led into preweighed bulb containing cupric oxide, which was kept hot. The steam produced in the reaction was absorbed in preweighed bulbs containing KOH and P_4O_{10}. The cupric oxide bulb, KOH bulb and the P_4O_{10} bulbs were weighed after the experiment. From an analysis of these weight changes it was possible for Dumas to determine the composition of water accurately.

Before experiment: weight of the CuO bulb = x gram
sum of the weights of KOH and P_4O_{10} bulbs = y gram

After experiment: weight of the CuO bulb = x′ gram
sum of the weights of KOH and P_4O_{10} bulbs = y′ gram

Therefore the amount of oxygen released as a result of the reduction of the cupric oxide = $(x-x')$ gram

Weight of the water produced = $(y'-y)$ gram

weight of the hydrogen taking part in the reaction = $(y'-y)-(x-x')$ gram

The ratio of hydrogen: oxygen = $[(y'-y)-(x-x')]/(x-x')$

The experimental ratio obtained by Dumas was $1{:}7.98 \simeq 1{:}8$.

From other independent experiments it is known that the atomic weights of hydrogen and oxygen are 1 and 16 respectively. Therefore, since one molecule of water has to have at least one atom of oxygen the weight ratio that follows is 2:16 i.e. the formula of water comes out to be H_2O.

27.4. DETERMINATION OF COMPOSITION OF AIR

27.4.1. Volumetric Procedure : A U-shaped eudiometer tube (Fig. 27.2) is used for the purpose. One arm of the eudiometer tube is closed and graduated. This closed end has two platinum wires sealed into the tube for the purpose of connecting to high voltage source and thus pass a spark through the gas mixture in the tube. The other arm has a short side tube provided with a stop-cock in order to regulate the volume of mercury taken in the eudiometer.

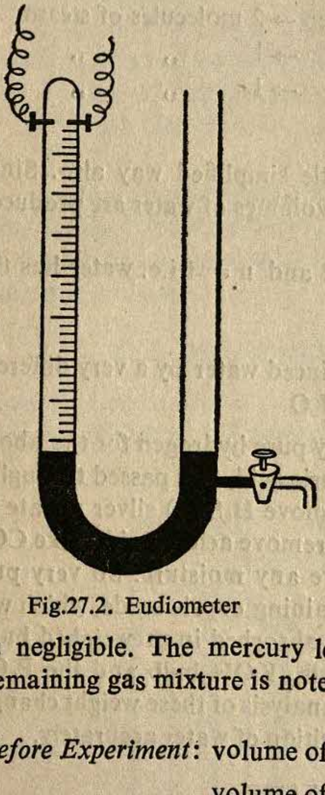


Fig.27.2. Eudiometer

Air is first led through KOH solution to remove any CO_2 and moisture. The tube is first evacuated and then some air is forced into the closed graduated arm of the eudiometer. By levelling the mercury columns in the two arms the volume of the dry, CO_2 free air is noted. Now pure dry hydrogen gas of nearly the same volume of air is introduced into the tube and volume read after adjusting the mercury columns in the two arms. Electric spark is now passed through the mixture of air and hydrogen which results in the formation of water. Compared to the volume of oxygen and hydrogen the volume of liquid water is negligible. The mercury levels are again adjusted and the volume of the remaining gas mixture is noted.

Before Experiment: volume of dry CO_2 free air = x ml.

volume of dry CO_2 free air + hydrogen = y ml.

volume of hydrogen = (y — x) ml.

After Experiment: volume of nitrogen and excess hydrogen = z ml.

reduction in volume = (y—z) ml.

Reduction in volume is due to the formation of water. We know that 2 volumes of hydrogen and 1 volume of oxygen produce water. The reduction in volume stands for the total reacting volumes of hydrogen and oxygen. Since out of a total of 3 reacting volumes oxygen is one-third we can write:

Volume of oxygen reacted = (y — z)/3

Since this volume of oxygen has come from x ml of air we can write:

Volume of oxygen per ml. of air = $(y - z)/3x$

Percentage of oxygen in dry air = $\frac{(y - z) \times 100}{3x}$

Actual experiments show that air contains about 22% oxygen and 78% nitrogen. However we have seen in Chapter 22 that this nitrogen also carries alongwith it small percentage of the noble gases.

27.4.2. Gravimetric Procedure : Dumas used his technique of determination of the composition of water with little alterations for the determination of the composition of air. Air was first passed through a KOH bulb to absorb CO_2 and then again through U-tubes of KOH and anhydrous $CaCl_2$ to absorb any moisture. The perfectly dried and CO_2 free air was then passed through a combustion tube containing copper. The combustion tube is connected through a stop-cock to a bulb. The combustion tube and the U-tube containing KOH and $CaCl_2$ were also joined through a stop-cock. Both the combustion tube and the bulb were evacuated prior to the start of the experiment and were weighed. The unreacted nitrogen gas was collected in the bulb placed after the combustion tube. The combustion tube and the bulb containing nitrogen were weighed again after the experiment.

Before the experiment: weight of the evacuated bulb = x gram
weight of the cumbustion tube = y gram
(with copper powder)

After the experiment: weight of the bulb plus nitrogen = x′ gram
weight of the combustion tube plus the bulb = z gram
(Note that some nitrogen will also remain trapped in the combustion tube)
weight of the combustion tube after evacuation = y′ gram

Therefore weight of the oxygen reacting with copper powder = $(y'-y)$ gram
Weight of the nitrogen in the bulb = $(x'-x)$ gram
weight of the air = weight of the oxygen plus the weight of the nitrogen
= $z-(x+y)$ gram
weight of the total nitrogen = weight of air minus the weight of oxygen
= $[z-(x+y)-(y'-y)] = (z-x-y')$ gram
The ratio of nitrogen to oxygen in air = $N_2 : O_2 = (z-x-y') : (y'-y)$
Experimental ratio obtained by Dumas was $N_2 : O_2 = 78 : 22$ per cent.

27.5. DETERMINATION OF THE FORMULA OF OZONE

In Chapter 20 we had already observed that on the passage of silent electric discharge through oxygen we get ozone. In order to determine the formula of this gas we have to be able to determine the amount of ozone formed during treatment of oxygen by silent electric discharge. Fortunately turpentine oil very readily absorbs ozone. Thus the consequent reduction in volume of the initial oxygen will give us an idea about how much oxygen has been converted into ozone.

A special equipment developed by Newth (Fig. 27.3) is used for the purpose. Two tubes one fitting properly into another are used. The inner tube carries dilute H_2SO_4 and a platinum wire. The outer tube is provided with a stop-cock at the bottom for evacuation and introduction of pure oxygen. This outer tube is connected near its upper end with a mercury manometer for reading the pressure. Both the inner and the outer tubes are provided with glass projections so arranged that they can hold in place a small tube containing turpentine oil. Pure oxygen is taken in the annular space between the two tubes. This set-up is now lowered into a vessel containing dilute H_2SO_4 into which there is another platinum wire. The platinum wires are now connected to the induction coil and silent electric discharge is passed. This results in the formation of ozone. There is a contraction in volume which is read with the help of the rise in the mercury column. Now the tube of turpentine oil is broken by rotating the two tubes—one against the other. The turpentine oil absorbs the ozone that has been formed. A second contraction occurs and this is read again with the help of the manometer.

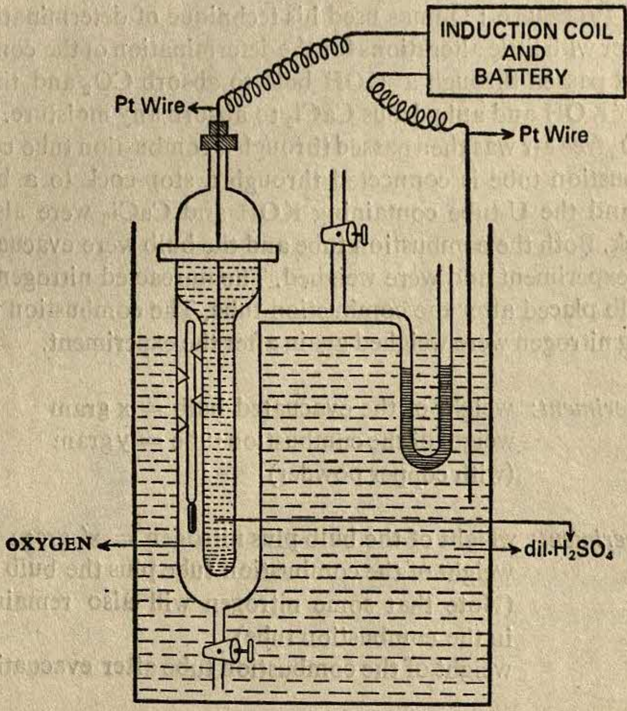


Fig. 27.3. Newth's apparatus for the determination of the formula of ozone

Let us assume that the first contraction after the passage of silent electric discharge is *n*. Let the second contraction be *m*. Thus the volume of ozone formed is *m*. Newth had made sure through several experimentations that the value *m* was always double the value of *n*. We started with pure oxygen and hence ozone must have been formed from pure oxygen only. So we may write O_x as the molecular formula of ozone. Then since the total number of oxygen atoms have to be conserved in such conversion we can safely write:

$2O_x = xO_2$ (total number of oxygen atoms
on both sides being the same 2x

Using Avogadro hypothesis one O_x molecule and O_2 molecule must occupy the same volume. Therefore the reduction in volume during the formation of ozone must be equal to (x—2) ml. Thus we can express the results of Newth's experiment as:

$$\frac{n}{m} = \frac{x-2}{2} = \frac{1}{2} \text{ (Newth found } m = 2n\text{)}$$

Therefore $x = 3$ and hence the formula of ozone is O_3.

27.6. DETERMINATION OF THE FORMULA OF AMMONIA

The determination procedure makes use of the oxidation of ammonia by chlorine gas to nitrogen and consequent reduction of chlorine to hydrogen chloride. In this procedure an aqueous solution of ammonia is used in excess so that the hydrogen chloride is converted to ammonium chloride because of ammonia being in excess.

A graduated (Fig 27.4) tube is provided with stop-cocks at both ends. The stop-cock at the upper end is connected to a funnel in which is taken the aqueous solution of ammonia. The tube is first evacuated and then filled with chlorine gas at ordinary temperature and pressure. The ammonia solution is added little by little to the chlorine gas. The reaction is very vigorous and causes flashes from time to time. In order to get all the chlorine used up some ammonia is added in excess. The ammonia remaining in the funnel is then removed. Little H_2SO_4 is added into the tube to react with the excess of ammonia. The graduated tube is now dipped into water and the lower stop-cock opened. It is observed that water rushes in and fills the graduated tube upto two-thirds. This water insoluble gas was determined to be nitrogen. The entire chlorine has undergone reaction to produce hydrogen chloride. It is known from other independent experiments that equal volumes of hydrogen and chlorine react to form twice the volume of hydrogen chloride. Thus three parts chlorine must have reacted with three parts by volume of hydrogen. This experiment proves that in ammonia there are 1 part of nitrogen and three parts of hydrogen,

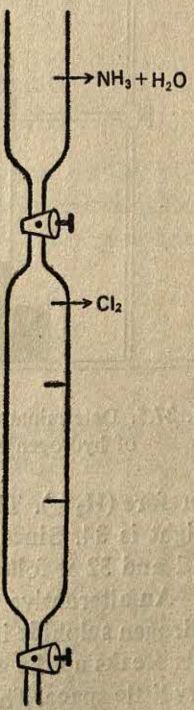


Fig. 27.4. Determination of the formula of NH_3

According to Avogadro hypothesis in one molecule of ammonia there must be present at least one atom of nitrogen and three atoms of hydrogen since both nitrogen and hydrogen are diatomic. Thus empirical composition of ammonia is $(NH_3)_x$. Vapour density of ammonia gas is known to be 8.5 so that molecular weight is 17. The atomic weights of nitrogen and hydrogen are known as 14 and 1 so that the value of x is 1. Thus the chemical formula of ammonia is NH_3. The following reaction takes place:

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

Addition of excess ammonia forms NH_4Cl.

27.7. DETERMINATION OF THE FORMULA OF HYDROGEN SULPHIDE

Several pieces of pure tin are taken in the bent portion of a hard glass tube as shown in Fig 27·5. The tube is first evacuated and then filled with pure hydrogen sulphide gas and is clamped in upright position over mercury. The level of mercury in the tube is marked. The bent portion of the tube containing tin is heated from outside when tin sulphide SnS/SnS_2 are produced. The tin sulphides are solid and hence occupy negligible space. Such an experiment leads to evolution of hydrogen whose volume is the same as that of hydrogen sulphide. This conclusion is reasonable because of the fact that there is no change in volume due to the reaction. Thus hydrogen sulphide contains its own volume of hydrogen. According to Avogadro hypothesis therefore one molecule of hydrogen sulphide must contain two atoms of hydrogen. The empirical composition of hydrogen sulphide is therefore (H_2S_x). The vapour density of the gas is 17. This means its molecular weight is 34. Since the atomic weights of hydrogen and sulphur are known to be 1 and 32 it follows that the value of x is 1.

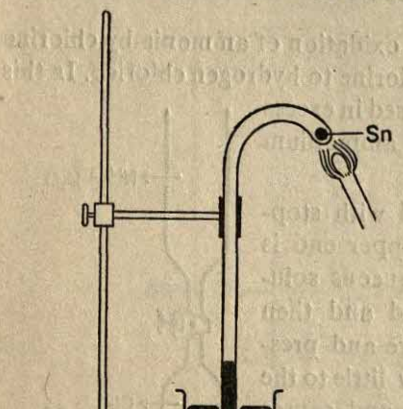


Fig. 27.5. Determination of the formula of hydrogen sulphide

An alternative way to determine the formula is to take a known volume of hydrogen sulphide in an eudiometer tube and pass electric spark through the gas. This breaks up the gas into hydrogen and sulphur. The latter being solid occupies very little space. The volume of hydrogen is found to be the same as the original hydrogen sulphide. So hydrogen sulphide contains its own volume of hydrogen. Thus one mole of H_2 must be coming from one mole of H_2S_x. Now vapour density will allow us to evaluate the value of x to be 1 as argued above.

27.8. DETERMINATION OF THE FORMULA OF CARBON DIOXIDE

The basic principle involved in the determination of the formula of carbon dioxide is to completely burn out a weighed amount of carbon in a stream of pure oxygen. Care is taken so that no carbon monoxide is formed. For this purpose the evolved gas is allowed to pass through heated cupric oxide so that any carbon monoxide is converted to carbon dioxide.

Inside a silica tube is taken a weighed amount of carbon in a small porcelain boat. Major portion of the silica tube is packed with cupric oxide placed close to the porcelain boat. The tube is kept heated. The silica tube is connected to a weighed KOH bulb to arrest the issuing carbon dioxide.

Before the experiment: weight of carbon = x gram
weight of KOH bulb = y gram

After the experiment: weight of carbon = 0 gram
weight of KOH bulb = y′ gram

Therefore the weight of carbon dioxide = y′—y = z gram
Therefore the weight of oxygen = (z—x) gram
Weight ratio C: O = x: (z—x)
Actual experiments give this ratio as 1 : 2.671
Dividing by the respective atomic weights we get the atom ratio:

$$C : O = (1/12) : (2.671/16) = 0.083 : 0.166 = 1 : 2$$

The empirical formula of carbon dioxide is thus $(CO_2)x$. Vapour density of the gas is 22 which means its molecular weight is 44. Taking the atomic weights of carbon and oxygen as 12 and 16 it is easily seen that x turns out to be 1. So the real chemical formula of carbon dioxide is CO_2.

27.9. DETERMINATION OF THE FOURMULA OF CARBON MONOXIDE

A graduated eudiometer provided with platinum sparking connections and a stopcock at the lower portion of the other arm (Fig. 27.2) is used. Pure carbon monoxide is taken into the closed graduated arm of the tube and its volume is read by adjusting the mercury columns in the two arms. Excess of pure dry oxygen is next introduced and its volume noted. Electric spark is now passed through the mixture till there is no further change in volume. This volume is noted, which is the sum of the volumes of carbon dioxide formed and remaining oxygen. Strong KOH solution of known volume is added and the carbon dioxide absorbed. The eudiometer should now have only excess unreacted oxygen. From a knowledge of this volume and the original volume of oxygen we know the volume of oxygen participating in the reaction. The contraction in volume on KOH treatment gives a measure of the carbon dioxide formed. Experimentally it is found that *x* ml. of carbon monoxide reacts with $\frac{1}{2}x$ ml. of oxygen to generate x ml. of carbon dioxide. According to Avogadro hypothesis this means 1 molecule of carbon monoxide reacts with $\frac{1}{2}$ molecule i.e. 1 atom of oxygen to give 1 molecule of carbon dioxide. We have already learnt that the formula of carbon dioxide is CO_2. So the formula of carbon monoxide is:

$$CO_2 - \tfrac{1}{2}O_2 = CO_2 - O = CO$$

27.10. DETERMINATION OF THE FOURMULA OF SULPHUR DIOXIDE

The principle involved is to burn some sulphur in a known volume of excess oxygen and to compare the volume of sulphur dioxide formed with that of the oxygen. The reaction is carried out in a graduated eudiometer tube of a special pattern (Fig. 27.6). The open end is provided with a stop-cock near the lower part of the arm. The other arm is joined to a big sized bulb with a mouth. The mouth is provided with a stopper through which passes two copper wires. One of these two copper wires is sealed to a copper spoon which holds some pure sulphur. The other copper wire is joined to a platinum wire which in turn reaches the spoon. The bulb and a part of the eudiometer tube is filled with pure dry oxygen and the level of the gas is noted by adjusting the mercury levels in the two arms. The copper wires are then connected to electric mains. The platinum wire gets heated up and initiates burning of sulphur in excess oxygen. After the burning of sulphur the eudiometer tube is allowed to cool down to room temperature. It is noted that there is no change in the volume of the gas as compared to the original volume of oxygen. Thus one molecule of oxygen produces one molecule of sulphur dioxide. In other words 1 molecule of sulphur dioxide is obtained from 1 molecule i.e. 2 atoms of oxygen. So the empirical formula of sulphur dioxide is S_xO_2. Vapour density of the gas is 32 i.e. its molecular weight is 64. Taking the respective atomic weights of sulphur and oxygen as 32 and 16 we can easily see that the value of x comes out to be 1. Thus the real chemical formula of sulphur dioxide is SO_2.

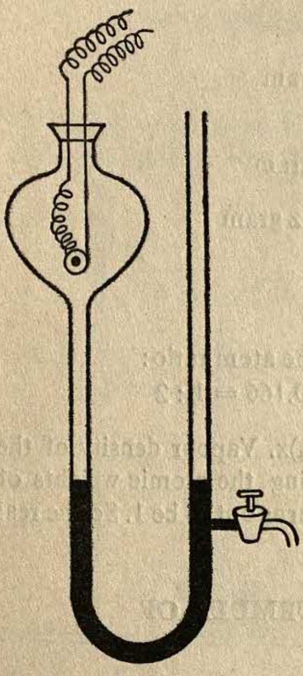


Fig. 27.6. Eudiometer for determination of the formula of sulphur dioxide

27.11. DETERMINATION OF THE FORMULA OF NITRIC OXIDE

An ordinary eudiometer tube (Fig. 27.2) provided with a heating spiral of nickel wire is taken for the purpose. Pure nitric oxide is taken in the graduated arm of the eudiometer which also has the heating nickel spiral. The volume of the gas is noted. The terminals of the nickel spiral are connected to a source of current. The nickel spiral gets heated and there begins a contraction in volume of the gas. At the end the eudiometer tube is cooled to room temperature and the volume of the gas is read to be half of the volume of nitric oxide. This gas is found to be nitrogen only. The nickel is converted to nickel oxide.

According to Avogadro hypothesis 1 molecule of nitric oxide contains $\frac{1}{2}$ molecule i.e. 1 atom of nitrogen. Thus we can write the formula of nitric oxide as NO_x. Vapour density of the gas is 15 i.e. its molecular weight is 30. Taking the respective atomic weights into consideration the value of x comes out to be 1. Therefore the chemical formula of nitric oxide is NO.

EXERCISES

1. Describe how you would arrive at the formula of water by adopting a volumetric procedure and a gravimetric procedure.

2. Describe Newth's technique of the determination of the formula of ozone.

3. How can we determine the percentage of air and nitrogen in air? Does the nitrogen of air contain nitrogen alone?

4. Describe procedures for determining the formulas of the following compounds :
(*a*) carbon dioxide (*b*) hydrogen sulphide (*c*) sulphur dioxide (*d*) nitric oxide

CHAPTER 28

QUALITATIVE ANALYSIS

28.1. INTRODUCTION

In this and the next Chapter we will discuss qualitative and quantitative analyses, which form an integral part of the inorganic chemistry curricula. This Chapter deals with the qualitative analyses of some selected metal ions and anions while the next Chapter takes up the quantitative analyses of cations and anions. In the qualitative analyses solubility and solubility products as also common ion effect play dominant role. Depending on the solubilities of the chlorides, the sulphides in acid and ammoniacal media, the hydroxides and the carbonates it has been possible to separate many metal ions in a number of groups. These qualitative groups, of course, have nothing to do with the groups of the periodic table. While the periodic groups are based on electron distribution the qualitative groups are based on the solubility of different salts. We have five groups in the qualitative scheme: Groups I, II, III, IV and V. Of these groups II and III are further subdivided into IIA and IIB, IIIA and IIIB. Unfortunately there is no such solubility scheme available for anions. Hence for anions there is no systematic approach. Special methods are adopted in particular cases.

28.2. DRY TESTS FOR SOME CATIONS AND ANIONS

Before one passes on to tests for the presence or absence of certain cations and anions in solution phase it is rewarding to spend some time for dry tests. Some important clues are sometimes available which might be of some assistance at a later stage of the analyses. Short discussion is presented below on three different types of dry tests.

28.2.1. Flame Test: Essential principle involved in this test is this: chlorides of some elements are readily decomposed when held at the outer tip of a blue Bunsen flame. Usually a clean platinum wire sealed at the end of a glass rod is dipped first in concentrated HCl, then a minute amount of the salt is taken on the platinum wire and the sample presented to the Bunsen flame. Heat decomposes the salt and the concerned metal atom gives its atomic spectra. The outer electrons are excited by the Bunsen flame and are raised to higher energy level. When the excited electrons drop down to their ground state the energy is released. If the energy released is within the visible region of the spectrum then we see the flame coloured. There are some elements which give characteristic colour. In Table 28.1 we depict the colours of some metals.

Table 28.1. Characteristic colours of metal in the Bunsen flame

Colour (with naked eye)	Colour (with cobalt glass)	Metal
1. Bright golden	1. Colourless	1. Sodium
2. Violet	2. Red violet	2. Potassium
3. Transient brickred	3. Light green	3. Calcium
4. Crimson red	4. Purple	4. Strontium
5. Light apple-green	5. Bluish green	5. Barium
6. Green	6. ——	6. Copper or Borate

Young learners should note that lead, arsenic and bismuth salts give bluish white colour but these ions poison the costly platnum wire. Tests with such elements should be avoided as far as practicable.

28.2.2. Borax Bead Test: Some transition metal ions give coloured metaborates. This property may be utilised in favourable cases for the qualitative detection of these metal ions. A loop is made with a platnum wire fused at the end of a glass rod. Some borax is taken in the loop and heated in the blue Bunsen flame. The borax loses its hydrate water and swells and finally gives a clear colourless bead. A little of the sample is taken on the bead and is then heated first in the reducing flame and then in the oxidising flame and the colour of the bead noted. The following type of reactions occur:

$$Na_2B_4O_7.10H_2O \rightarrow 2NaBO_2 + B_2O_3 + 10H_2O$$
$$CuO + B_2O_3 \rightarrow Cu(BO_2)_2 \text{ (blue)}$$

Colours of the other borates are: $Co(BO_2)_2$ deep blue; $Cr(BO_2)_3$ green; $Fe(BO_2)_2$ light green; $Fe(BO_2)_3$ brown: $Ni(BO_2)_2$ yellowish brown. There is no point in trying borax bead test unless the sample is itself coloured. Table 28.2 records the colours of some metal metaborates.

Table 28.2. Colours of Borax Beads of Some Metal Ions

Colour in reducing flame	Colour in oxidising flame	Metal
1. Green in both hot and cold condition	1. Green in both hot and cold condition	1. Chromium
2. Red in cold condition	2. Green while hot but blue in the cold	2. Copper
3. Green in both hot and cold condition	3. Reddish yellow while hot but yellow in the cold	3. Iron
4. Deep blue in both hot and cold condition	4. Deep blue in both hot and cold condition	4. Cobalt
5. Light brown in both hot and cold condition	5. Yellowish brown while hot	5. Nickel
6. Almost colourless in both hot and cold condition	6. Light rose coloured	6. Manganese

28.2.3. Cobalt Nitrate Test: This test should be performed only if the sample is colourless. The sample is mixed with Na_2CO_3 and heated on a charcoal block with a blow-pipe. If a colourless residue is left behind then it is moistened with a drop or two of cobalt nitrate solution and again heated with a blow-pipe. On cooling the colour is noted. Some metal ions like, zinc, aluminium and manganese, form characteristic mixed oxides:

$$ZnSO_4 + Na_2CO_3 \rightarrow ZnO + CO_2 + Na_2SO_4$$

$$2Co(NO_3)_2 \rightarrow 2CoO + 4NO_2 + O_2$$

$$ZnO + CoO \rightarrow ZnCoO_2 \quad \text{(green; Rinmann's green)}$$

$$Al_2O_3 + CoO \rightarrow Al_2CoO_4 \quad \text{(blue; Thenard's blue)}$$

In this test too much cobalt nitrate must be avoided as the whole mass might turn black due to excessive cobalt oxide. Table 28.3 records the colours and inferences drawn from cobalt nitrate test.

Table 28.3. Cobalt Nitrate Test and Metal Ions

Observations of cobalt nitrate test	Metal
1. Green residue	1. Zinc
2. Blue residue (infusible)	2. Aluminium
3. Blue residue (fusible)	3. Borate, silicate, phosphate, or arsenate
4. Light pink residue	4. Mangnesium

28.2.4. Heating in a Dry Test Tube: The sample is taken in a clean and dry test tube. It is held in a slanting position over a Bunsen flame and then gradually heated and the observations carefully noted. Such heating generally leads to three distinct types of changes: (a) a change in colour of the sample (b) sublimation of the whole or part of the sample and (c) evolution of gas. It is often possible to have some preliminary idea about the composition of the sample. Table 28.4, 28.5 and 28.6 record these observations and the inferences that can be drawn therefrom.

Table 28.4. Change of Colour on Heating

Change in colour	Metal
1. Yellow when hot, colourless when cold	1. Zinc (oxide)
2. Brown in both hot and cold condition	2. Cadmium (oxide)
3. Deep red while hot but deep brown when cold	3. Iron (oxide)
4. Yellowish brown while hot but yellow when cold	4. Lead (oxide) Tin (oxide) Bismuth (oxide)
5. Turns black	5. Copper, nickel or manganese

Table 28.5. Sublimation on Heating and Inferences

Tests and Observations	Inferences
I. WHITE SUBLIMATE	$HgCl_2$, $HgBr_2$, Hg_2Cl_2, As_2O_3 Sb_2O_3 and ammonium halides
1. White sublimate taken up in water and treated with H_2S and warmed ; black HgS	1. $HgCl_2$ or Hg_2Cl_2
2. During sublimation garlic odour is given off and on treatment with H_2S yellow precipitate (As_2S_3) is obtained	2. As_2O_3
3. Sublimate treated with H_2S gives orange coloured (Sb_2S_3) precipitate	3. Sb_2O_3
4. White sublimate but no change on treatment with H_2S	4. Ammonium halides
II. COLOURED SUBLIMATE	HgS, HgI_2, I_2, As_2S_3
1. Black sublimate turns red on rubbing	1. HgS
2. Yellow sublimate turns rose on rubbing	2. HgI_2
3. Violet sublimate	3. I_2
4. Yellow sublimate	4. As_2S_3

Table 28.6. Evolution of gas and Inferences

Observations on heating	Inferences
1. Evolved colourless gas turns lime water milky	1. Carbonate/Bicarbonate
2. Colourless pungent smelling gas, turns red litmus paper blue and mercurous nitrate paper black	2. Ammonium salts
3. Colourless gas, smells like rotten eggs, turns lead acetate paper black	3. Sulphide
4. Colourless gas, smells of burning sulphur and turns acidified dichromate solution from orange to green	4. Sulphite/Thiosulphate
5. Brown coloured gas	5. Nitrite, nitrate or bromide
6. Violet vapour condensing at the upper cooler portion of the test tube as black looking crystals	6. Iodide
7. Light yellowish green gas, turns starch-iodide paper blue	7. Easily decomposable chloride or chloride mixed with some oxidising agent

28.3. CLASSIFICATION OF METAL IONS

Table 28.7 gives a classification of as many as twentyeight metal ions in different qualitative groups. The Table indicates the group reagent that precipitates the particular metal ions. The composition of the different precipitates has also been indicated.

Table 28.7. Classification of Metal ions in Qualitative Groups

Group	Reagent	Metal ions	Precipitates	Properties of the precipitates
I	dilute HCl	Ag^+, Pb^{2+}, Hg_2^{2+}	$AgCl$, $PbCl_2$ Hg_2Cl_2	Chlorides of these ions are insoluble in dil. HCl in the cold.
II (A+B)	warm dilute HCl plus H_2S	Hg^{2+}, Pb^{2+}, Bi^{3+} Cu^{2+}, Cd^{2+}, As^{3+} Sb^{3+}, Sn^{2+}, As^{5+} Sb^{5+} and Sn^{4+}	HgS, PbS, Bi_2S_3 CuS, CdS, As_2S_3, Sb_2S_3, SnS, As_2S_5 Sb_2S_5, SnS_2	Sulphides of these ions are insoluble in 0.3*N* HCl. Of these, HgS, PbS, Bi_2S_3, CuS and CdS are insoluble in yellow ammonium sulphide $(NH_4)_2S_x$. The remaining sulphides are soluble in $(NH_4)_2S_x$ Thus it is possible to separate group IIA (Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}) from Group IIB (Sn^{2+}, Sn^{4+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}).
IIIA	NH_4Cl plus dilute NH_4OH	Al^{3+}, Fe^{3+}, Cr^{3+}	$Al(OH)_3$, $Fe(OH)_3$ $Cr(OH)_3$	The solubility products of these hydroxides are quite low. In the presence of NH_4^+ common ion NH_4OH is rendered a still weaker base. But even then the solubility products of these hydroxides are exceeded and they are precipitated.

Table 28.7 (continued)

Group	Reagent	Metal ions	Precipitates	Properties of the precipitates
IIIB	NH_4Cl, NH_4OH plus H_2S	Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}	CoS, NiS, MnS ZnS	The solubility products of the hydroxides of these ions are greater than those of $Fe(OH)_3$, $Cr(OH)_3$ and $Al(OH)_3$. Hence their hydroxides are not precipitated by NH_4OH in presence of NH_4Cl. Solubility products of their sulphides are also greater than those of HgS, PbS, CuS etc. Hence they are precipitated by H_2S in presence of NH_4OH.
IV	NH_4Cl, NH_4OH plus $(NH_4)_2CO_3$	Ca^{2+}, Sr^{2+}, Ba^{2+}	$CaCO_3$, $SrCO_3$, $BaCO_3$	Carbonates of these three metal ions are insoluble in presence of NH_4Cl and NH_4OH.
V	No group reagent	Mg^{2+}, Na^+, K^+ NH_4^+		These metal salts remain in solution from the beginning of Group I upto the end of group IV. These ions are tested individually by special reagents.

28.4. REACTIONS OF METAL IONS OF GROUP I

Silver Ion: It gives a white gelatinous precipitate with dilute HCl. The precipitate is soluble in excess ammonia and can be reprecipitated by the addition of HNO_3:

$$AgNO_3 + HCl \rightarrow AgCl\downarrow + HNO_3$$

$$AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$$

$$[Ag(NH_3)_2]Cl + 2HNO_3 \rightarrow AgCl + 2NH_4NO_3$$

Silver ion also produces precipitates with KI, K_2CrO_4 and H_2S. The colours of AgI, Ag_2CrO_4 and Ag_2S are yellow, orange-red and black respectively.

Mercurous Ion: This ion gives a white precipitate of Hg_2Cl_2 in HCl solution. The precipitate is soluble in aqua regia—the mercurous ion being oxidised to the mercuric state:

$$Hg_2(NO_3)_2 + 2HCl \rightarrow Hg_2Cl_2\downarrow + 2HNO_3$$

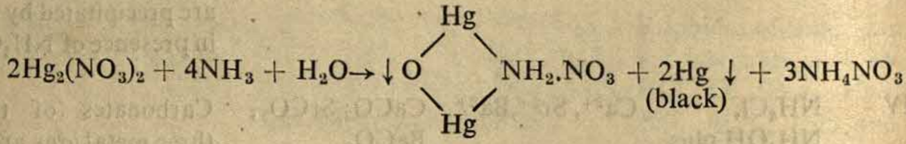
$$3Hg_2Cl_2 + 8HNO_3 \rightarrow 3HgCl_2 + 3Hg(NO_3)_2 + 2NO + 4H_2O$$

$$Hg_2Cl_2 + Cl_2 \rightarrow 2HgCl_2$$

The white Hg_2Cl_2 turns black in presence of ammonia:

$$Hg_2Cl_2 + 2NH_3 \rightarrow \underset{\substack{\text{(white}\\ \text{amidochloro}\\ \text{mercury (II))}}}{Hg(NH_2)Cl} + \underset{\text{(black)}}{Hg} + NH_4Cl$$

A black precipitate is also obtained on the addition of ammonia to a solution of mercurous nitrate:



$$2Hg_2(NO_3)_2 + 4NH_3 + H_2O \rightarrow \downarrow O\langle Hg_2\rangle NH_2.NO_3 + \underset{\text{(black)}}{2Hg\downarrow} + 3NH_4NO_3$$

Mercurous chloride reacts with Na_2CO_3 under heating to give mercury mirror:

$$2Hg_2Cl_2 + 2Na_2CO_3 \rightarrow 4Hg + 4NaCl + 2CO_2 + O_2$$

A precipitate of black mercury is also obtained during the reaction of Hg_2^{2+} ion with stannous chloride:

$$Hg_2(NO_3)_2 + SnCl_2 + 2HCl \rightarrow 2Hg\downarrow + SnCl_4 + 2HNO_3$$

Mercurous salts react with H_2S to give a precipitate of black HgS and Hg:

$$Hg_2(NO_3)_2 + H_2S \rightarrow 2HNO_3 + HgS\downarrow + Hg\downarrow$$

Lead Ion: A white precipitate of $PbCl_2$ is obtained with HCl. This precipitate is soluble in hot water but crystallises on cooling. Because of this solubility the entire lead is not precipitated in group I but is carried into group II, where it is precipitated as black PbS:

$$Pb(NO_3)_2 + 2HCl \rightarrow PbCl_2\downarrow + 2HNO_3;\ PbCl_2 + H_2S \rightarrow PbS + 2HCl$$

Lead ion gives glistening yellow crystalline precipitate with KI. This is soluble in excess of KI because of the formation of a tetraiodo complex:

$$Pb(NO_3)_2 + 2KI \rightarrow PbI_2\downarrow + 2KNO_3;\ PbI_2 + 2KI \rightarrow K_2[PbI_4]$$

With K_2CrO_4 a yellow insoluble precipitate of lead chromate is formed:

$$Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4\downarrow + 2KNO_3$$

Sulphuric acid gives an insoluble precipitate of $PbSO_4$. This precipitate is soluble in excess of ammonium acetate:

$$PbSO_4 + 2CH_3COONH_4 \rightarrow (CH_3COO)_2Pb + (NH_4)_2SO_4$$

Separation and detection of the group I elements are given in Table 28.8

Table 28.8. Analysis of Group I

<table>
<tr><td colspan="3">The mixture of the ions under analysis is treated with dilute HCl. The precipitate so obtained is filtered through a filter paper (Whatman No. 1). The precipi- is transferred into a small beaker, boiled with water and again filtered.</td></tr>
<tr><td colspan="2"><i>Residue</i>: The residue left on the filter paper may be Hg_2Cl_2 and AgCl. This is washed with hot water and the washing rejected. The residue is now treated with dilute NH_4OH.</td><td rowspan="2"><i>Filtrate</i>: May contain $PbCl_2$. It is tested with K_2CrO_4 or KI solution when a yellow precipitate is obtained. PbI_2 is soluble in hot water but not $PbCrO_4$.</td></tr>
<tr><td><i>Residue</i>: Mercurous mercury is indicated if there is a black precipitate on the filter paper. It is due to Hg plus $Hg(NH_2)Cl$.</td><td><i>Filtrate</i>: It is treated with HNO_3 till acidic. If a white precipitate appears silver (I) is indicated. The white precipitate of AgCl will be soluble again in NH_4OH.</td></tr>
</table>

28.5. REACTIONS OF METAL IONS OF GROUPS IIA AND IIB

Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+} are members of group IIA while As^{3+}/As^{5+}, Sb^{3+}/Sb^{5+} and Sn^{2+}/Sn^{4+} belong to group IIB. All these ions are precipitated as their sulphides from dilute HCl medium. Of these, sulphides of arsenic, antimony and bismuth are soluble in yellow ammonium sulphide (also called polysulphide). Thus the metals of the two subgroups can be separated by treatment with polysulphide. Below are given some typical individual reactions of these ions:

REACTIONS OF METAL IONS OF GROUP IIA:

Mercury (II) Ion: This ion reacts with H_2S in acidic medium rather slowly —first a whitish, then a yellow, then brown and finally black HgS is formed:

$$\begin{array}{c} 3HgCl_2 + 2H_2S \rightarrow \underset{\text{(whitish)}}{HgCl_2.2HgS} + 4HCl \\ \Big\downarrow H_2S \\ \underset{\text{(black)}}{3HgS} + 2HCl \end{array}$$

The black precipitate of HgS is not easily soluble in acids but dissolves in aqua regia:

$$3HgS + (2HNO_3 + 6HCl) \rightarrow 3HgCl_2 + 2NO + 3S + 4H_2O$$

The reaction of mercuric chloride with stannous chloride is indispensable in the volumetric estimation of iron. Ferric iron is reduced in 6*N* HCl medium by dropwise addition of $SnCl_2$ till the yellow colour of ferric chloride changes to light green or turns nearly colourless depending on the amount of iron. Little $SnCl_2$ is always added in excess. This excess $SnCl_2$ is removed by the addition of mercuric chloride to the cold solution of the ferrous iron. $HgCl_2$ is reduced to a silky white precipitate of Hg_2Cl_2. Too much excess of $SnCl_2$ may reduce the Hg_2Cl_2 to black Hg, which will spoil subsequent titration by permanganate or dichromate (Chapter 29).

$$Hg_2Cl_2 + SnCl_2 \rightarrow SnCl_4 + Hg_2Cl_2 \downarrow$$
$$Hg_2Cl_2 + SnCl_2 \rightarrow SnCl_4 + 2Hg_2 \downarrow$$

Reaction of mercuric ion with potassium iodide is also very important in qualitative analysis. First red HgI_2 is precipitated which dissolves in excess KI to give the colourless tetraiodo complex:

$$HgCl_2 + 2KI \rightarrow HgI_2 \downarrow + 2KCl$$
$$HgI_2 + 2KI \rightarrow K_2HgI_4$$

Addition of KOH to the above solution produces what is known as Nessler's reagent. This is an excellent reagent for the detection of ammonium ion. The ammonia gas liberated on heating an ammonium salt with alkali reacts with Nessler's reagent to give a brown coloured precipitate of variable composition:

$$NH_3 + 2K_2[HgI_4] + 3KOH \rightarrow \underset{\text{(brown precipitate)}}{[NH_2{-}Hg{-}O{-}Hg]\,I} + 7KI + 2H_2O$$

Mercuric chloride reacts with ammonia to give a white precipitate of $Hg(NH_2)Cl$. But mercurous chloride gives a black precipitate due to the formation of a mixture of $Hg(NH_2)Cl$ and Hg:

$$HgCl_2 + NH_4OH \rightarrow H_2N{-}Hg{-}Cl \downarrow + HCl + H_2O$$
$$Hg_2Cl_2 + 2NH_4OH \rightarrow H_2N{-}Hg{-}Cl \downarrow + Hg \downarrow + NH_4Cl + 2H_2O$$

Bismuth Ion: This ion is stable only when the medium contains enough acid. Addition of excess water to a bismuth solution produces a milky white turbidity due to hydrolysis to oxysalt:

$$BiCl_3 + H_2O \rightarrow BiOCl \downarrow + 2HCl$$

Sodium stannite, obtained by the reaction of $SnCl_2$ with excess NaOH, reduces bismuth salts to black metallic bismuth:

$$SnCl_2 + 4NaOH \rightarrow Na_2[SnO_2] + 2NaCl + 2H_2O$$
$$2BiCl_3 + 6NaOH + 3Na_2[SnO_2] \rightarrow \underset{\text{(black)}}{2Bi \downarrow} + \underset{\text{(stannate)}}{3Na_2[SnO_3]} + 6NaCl + 3H_2O$$

Cupric Ion: This ion is precipitated as CuS on the passage of H_2S through an acidified cupric solution. The precipitate is soluble in nitric acid. When copper is present alongwith iron for quantitative estimation copper is precipitated as CuS and removed by filtration. Thereafter it is dissolved in boiling HNO_3:

$$3CuS + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 3S \downarrow + 4H_2O$$

This solution can then be titrated iodometrically (Chapter 29). In excess ammonia copper develops a deep blue colour due to the formation of cuprammine complex:

$$2CuSO_4 + 2NH_4OH \rightarrow CuSO_4.Cu(OH)_2 + (NH_4)_2SO_4$$

$$CuSO_4.Cu(OH)_2 + 6NH_4OH + (NH_4)_2SO_4 \rightarrow 2[Cu(NH_3)_4]SO_4 + 8H_2O$$

The blue colour is destroyed by KCN and a colourless complex of cuprocyanide is formed:

$$2[Cu(NH_3)_4]SO_4 + 4KCN \rightarrow 2Cu(CN)_2 + 2K_2SO_4 + 8NH_3$$

$$2Cu(CN)_2 \rightarrow 2CuCN \downarrow + (CN)_2 \text{ (cyanogen gas)}$$

$$CuCN + 3KCN \rightarrow K_3[Cu(CN)_4] \text{ (colourless)}$$

The cuprocyanide complex has a very high stability constant i.e. it dissociates very little in solution. Thus H_2S cannot precipitate black Cu_2S from a cyanide solution of copper (I). On the other hand the cadmicyanide complex $[Cd(CN)_4]^{2-}$ is weak and dissociated in solution to give the precipitate of yellow CdS when allowed to react with H_2S. This is how copper and cadmium are separated and detected in group IIA.

Another very important reaction of cupric copper is with KI. The iodide ion reduces cupric copper to the cuprous state and liberates iodine which can be titrated quantitatively by a standard thiosulphate solution:

$$2CuSO_4 + 4KI \rightarrow 2CuI + I_2 + 2K_2SO_4$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Cadmium Ion: This ion reacts with H_2S to give a yellow precipitate of CdS. The solubility product of CdS is relatively high : HgS : $\sim 10^{-52}$; CuS : $\sim 10^{-45}$; CdS : $\sim 10^{-26}$. Thus in order to get the precipitate of CdS the solution has to be diluted properly to lower the acid concentration and thereby to raise the concentration of the sulphide solution.

In ammonia colourless tetrammine, $[Cd(NH_3)_4]^{2+}$, is formed and in excess cyanide we get $[Cd(CN)_4]^{2-}$. Its stability constant is low and hence it dissociates appreciably into ions. Thus passage of H_2S can give the yellow precipitate of CdS:

$$K_2[Cd(CN)_4] + H_2S \rightarrow CdS \downarrow + 2KCN + 2HCN$$

REACTIONS OF METAL IONS OF GROUP IIB :

Arsenious Ion: In dilute acid medium it is precipitated as yellow As_2S_3. This precipitate is soluble in yellow ammonium (poly) sulphide as thioarsenate:

$$As_2S_3 + 3(NH)_4)_2S_2 \rightarrow 2\,(NH_4)_3\,[AsS_4] + S \downarrow$$

Ammonium thioarsenate decomposes on the addition of HCl into arsenic pentasulphide:

$$2(NH_4)_3[AsS_4] + 6HCl \rightarrow As_2S_5 \downarrow + 3H_2S + 6NH_4Cl$$

Arsenious ion, As (III), does not produce any precipitate with magnesia mixture ($MgCl_2 + NH_4Cl + NH_4OH$). But pentavalent arsenic i.e. arsenate ion gives a white crystalline precipitate of magnesium ammonium arsenate with magnesia mixture ($MgNH_4AsO_4$).

Arsenic (Arsenate) Ion: It reacts slowly with H_2S as it is first reduced to arsenic (III) and is then precipitated as As_2S_3:

$$2H_3AsO_4 + 5H_2S \rightarrow As_2S_3 \downarrow + 2S \downarrow + 8H_2O$$

Arsenate ion can be reduced faster by SO_2 and threafter H_2S can give the As_2S_3 precipitate readily.

With magnesia mixture it readily gives the white precipitate of magnesium ammonium arsenate ($MgNH_4AsO_4$):

$$(NH_4)_2AsO_4 + MgCl_2 \rightarrow MgNH_4AsO_4 \downarrow + 2NH_4Cl$$

Antimony Ion: Antimony, like arsenic, can show two oxidation states: +3 and + 5. Its reactions are also parallel to those of arsenic. Antimony (III) reacts with H_2S to give orange precipitate of Sb_2S_3. This dissolves in excess ammonium polysulphide to give thioantimonate:

$$2SbCl_3 + 3H_2S \rightarrow Sb_2S_3 \downarrow + 6HCl$$
$$Sb_2S_3 + 3(NH_4)S_2 \rightarrow 2(NH_4)_3[SbS_4] + S \downarrow$$

The thioantimonate decomposes in acid to give first Sb_2S_5 and then Sb_2S_3:

$$2(NH_4)_2SbS_4 + 6HCl \rightarrow Sb_2S_5 \downarrow + 6NH_4Cl + 3H_2S$$
$$Sb_2S_5 \rightarrow Sb_2S_3 \downarrow + 2S \downarrow$$

The antimony salts also undergo hydrolysis in large excess of water to give precipitate of oxysalts:

$$SbCl_3 + H_2O \rightleftharpoons SbOCl \downarrow + 2HCl$$

Stannous Ion: It reacts with H_2S in dilute HCl medium to precipitate brown coloured SnS. This is soluble in yellow ammonium sulphide:

$$SnCl_2 + H_2S \rightarrow SnS \downarrow + 2HCl \; ; \; SnS + (NH_4)_2S_2 \rightarrow (NH_4)_2SnS_3$$

The thiostannate decomposes in HCl and gives the precipitate of yellow SnS_2:

$$(NH_4)_2SnS_3 + 2HCl \rightarrow SnS_2 \downarrow + 2NH_4Cl + H_2S$$

Stannous chloride reacts with excess sodium hydroxide to form a solution of sodium stannite:

$$SnCl_2 + 4NaOH \rightarrow Na_2[SnO_2] + 2NaCl + 2H_2O$$

Sodium stannite is a good reducing agent and can reduce bismuth (III) to black elementary bismuth:

$$2BiCl_3+6NaOH+3Na_2\,[SnO_2] \rightarrow 2Bi \downarrow +3Na_2\,[SnO_3]+6NaCl+3H_2O$$

Stannous chloride reacts with mercuric chloride to give a precipitate of Hg_2Cl_2 which can be reduced further to black mercury.

Stannic Ion: This is precipitated by H_2S as yellow SnS_2. This dissolves in polysulphide as thiostannate:

$$SnS_2 + (NH_4)_2S_2 \rightarrow (NH_4)_2SnS_3 \xrightarrow{HCl} SnS_2 \downarrow$$

There is no change with mercuric chloride. However it can be reduced by iron powder and thereafter the usual reactions with mercuric chloride are observed:

$$SnCl_4 + Fe \rightarrow SnCl_2 + FeCl_2$$

Separation of Group IIA and Group IIB: H_2S gas is bubbled through a solution of the ions of groups IIA and IIB maintained at 0.2 to 0.3*N* acidity. The precipitate is filtered and the filtrate is reserved for analyses of the later groups.

The precipitate of groups IIA and IIB is treated with yellow ammonium sulphide, $(NH_4)_2S_x$. The metal ions of group IIB dissolve out as the thiosalts while those of group IIA remain insoluble. The mixture is filtered. The filtrate is used for the analysis of group IIB and the precipitate for ions of group IIA. The separation methods are given in Tables 28.9 and 28.10.

Table 28.9. Analysis of Group IIA

<table>
<tr><td colspan="4">The precipitate of groups IIA and IIB sulphides is collected on filter paper. The filter paper is pierced and the precipitate collected in a beaker. 5–7 ml of yellow ammonium polysulphide is added and warmed to 50–60°C for a few minutes. The mixture is now filtered and the precipitate is washed with small volume of dilute polysulphide.</td></tr>
<tr><td colspan="2">Residue: May be HgS, PbS, Bi_2S_3, CuS and CdS. The precipitate is taken in a beaker and boiled with few ml. of 1:3 HNO_3 and filtered again.</td><td colspan="2">Filtrate: Reserved for analysis of group IIB. (Table 28.10)</td></tr>
<tr><td rowspan="3">Residue: May be only black HgS. This is dissolved in either (a) conc. HCl and Br_2 or (b) aqua regia. The excess bromine or acid is removed by heating. The remaining material is treated with water and then with $SnCl_2$. A white precipitate of Hg_2Cl_2 or a black precipitate of Hg indicates mercury.</td><td colspan="3">Filtrate: May be Pb (II), Cu (II), Bi (III) and Cd (II). A small portion is treated with dilute H_2SO_4 plus ethyl alcohol. If Pb (II) is present a white precipitate of $PbSO_4$ is obtained. If Pb (II) is present then the entire filtrate is treated with 1:1 H_2SO_4 and heated to dense white fumes. It is cooled, diluted and filtered.</td></tr>
<tr><td rowspan="2">Residue: White $PbSO_4$. It is soluble in ammonium acetate. A drop or two of acetic acid is added, followed by K_2CrO_4 solution. A yellow precipitate of $PbCrO_4$ indicates lead (II).</td><td colspan="2">Filtrate: May contain Bi (III), Cu (II) and Cd (II). It is treated with excess ammonia and filtered.</td></tr>
<tr><td>Residue: White precipitate of Bi $(OH)_3$. It turns black on the addition of sodium stannite</td><td>Filtrate: May be Cu(II) and Cd(II). If the solution is blue it is divided in two parts:
1. One part is acidified with acetic acid and then $K_4Fe(CN)_6$ added. A brown red precipitate of $Cu_2Fe(CN)_6$ indicates copper (II)
2. KCN is added dropwise to discharge the blue colour. A yellow precipitate with H_2S indicates Cd (II).</td></tr>
</table>

Table 28.10. Analysis of Group IIB

The entire precipitate of groups IIA and IIB is treated with yellow ammonium polysulphide at 50–60°C for a few minutes and filtered. The filtrate contains group IIB ions as thiosalts. This solution is treated with some water and acidified with dilute HCl. The tri- and pentasulphides of arsenic, antimony and disulphide of tin are then precipitated. After washing with H_2S water we are left with As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5 and SnS_2. Some sulphur also accompanies the precipitates. The precipitates are boiled with 5-10 ml of concentrated HCl, diluted with little water and filtered.

<table>
<tr>
<td rowspan="2">*Residue*: May be As_2S_3/As_2S_5. This is treated with dilute ammonia and H_2O_2 (5 ml. of 3% solution). After warming for a while the solution is cooled and treated with magnesia mixture. If arsenic is present colourless crystalline precipitate of $MgNH_4AsO_4 . 6H_2O$ is obtained.
The above solution of the arsenate reacts with $AgNO_3$ to precipitate brown Ag_3AsO_4.</td>
<td colspan="2">*Filtrate*: May contain ($SbCl_4^-$ and $(SnCl_6)^{2-}$ The solution is divided into two parts:</td>
</tr>
<tr>
<td>1. The first part is made slightly ammoniacal. Then 2-3 ml of oxalic acid is added to convert tin (II) to an oxalato complex. On passing H_2S tin (II) remains unaffected but Sb (III) is precipitated as orange Sb_2S_3.</td>
<td>2. The second portion is partly neutralised. A pinch of iron powder is added and the solution warmed to reduce tin (IV) to tin (II). The solution is filtered and the filtrate treated with $HgCl_2$. A white precipitate indicates tin.</td>
</tr>
</table>

28.6. REACTIONS OF METAL IONS OF GROUPS IIIA AND IIIB

Group IIIA includes the ions iron (III), chromium (III) and aluminium (III) while group IIIB carries cobalt (II), nickel (II), manganese (II) and zinc (II). The elements of group IIIA are precipitated as their trivalent hydroxides, $M (OH)_3$, by NH_4OH even in the presence of the common ion containing NH_4Cl. We have already seen that the solubility products of these hydroxides are quite low. On the other hand the solubility products of the hydroxides of the group IIIB metals, $M(OH)_2$, are rather high and hence they are not precipitated by NH_4OH in the presence of NH_4Cl. It should be noted that these hydroxides will be precipitated in the absence of NH_4Cl because then their solubility products are exceeded by the presence of NH_4OH alone. The group IIIB ions are precipitated as their sulphides on the passage of H_2S through their solution in NH_4OH and NH_4Cl. Thus it is possible to separate the two subgroups: precipitating the IIIA metal ions as their hydroxides and IIIB ions as their sulphides. Some individual reactions of these ions are now discussed.

Reactions of Metal Ions of Group IIIA

Ferrous Ion: There is no precipitation of ferrous hydroxide on the addition of NH_4OH in the presence of NH_4Cl. However if H_2O_2 is added then ferrous is oxidised to ferric and brown precipitate of $Fe(OH)_3$ is formed. In the absence of H_2O_2 and NH_4Cl addition of ammonia gives a dirty green precipitate of ferrous hydroxide:

$$FeSO_4 + 2NH_4OH \rightarrow Fe(OH)_2 \downarrow + (NH_4)_2SO_4$$
$$2Fe(OH)_2 + 2H_2O_2 \rightarrow 2Fe(OH)_3 \downarrow + H_2O + \tfrac{1}{2}O_2$$

Ferrous ion reacts with potassium ferricyanide to give deep coloured Turnbull's blue precipitate (Chapter 23):

$$FeSO_4 + K_3Fe(CN)_6 \rightarrow KFe[Fe(CN)_6] \downarrow + K_2SO_4$$

There is no special colour formation with thiocyanate, although ferric ion gives a blood red colouration. However ferrous iron gives a very distinctive intense red colour with ortho-phenanthroline. A tris chelate is formed in the process (Fig. 28.1). With ferric iron a light blue colour is formed:

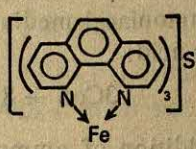


Fig. 28.1. Tris (ortho-phenanthroline) iron (II) sulphate

Ferric Ion : Even in the presence of NH_4Cl there appears a brown precipitate of $Fe(OH)_3$ on the addition of NH_4OH. This precipitate is utilised in the volumetric as well as the gravimetric determination of iron. The precipitate is filtered through a quantitative paper, washed with ammonium nitrate solution and finally ignited in a crucible to the Fe_2O_3 state. This is the basis of the gravimetric estimation. For the volumetric estimation the washed precipitate is dissolved in hot $6N$ HCl, reduced with $SnCl_2$, cooled and the excess $SnCl_2$ removed by the addition of $HgCl_2$. Thereafter the solution is diluted with $2N$ H_2SO_4, phosphoric acid added and the solution titrated by a standard solution of $K_2Cr_2O_7$ using diphenylamine sulphonate as indicator. Volumetric estimation may also be carried out by a standard solution of $KMnO_4$ using Zimmermann-Reinhardt preventive solution (Chapter 29).

Potassium thiocyanate gives a blood red colour—the exact formula is not known with certainty. However we may write it as $Fe(NCS)_x(H_2O)_{6-x}$ complex. The colour is destroyed on the addition of excess fluoride ion due to the formation of $[FeF_6]^{3-}$.

With potassium ferrocyanide deep Prussian blue precipitate $KFe[Fe(CN)_6]$ is obtained.

Chromic Ion: In the presence of NH_4Cl, addition of NH_4OH gives a light green gelatinous precipitate of $Cr(OH)_3$. On boiling with Na_2O_2 the precipitate gets oxidised to the soluble yellow chromate ion:

$$2Cr(OH)_3 + 3Na_2O_2 \rightarrow 2Na_2CrO_4 + 2NaOH + 2H_2O$$

The yellow chromate solution may be acidified with H_2SO_4, cooled, H_2O_2 added and the solution shaken with a few ml. of amyl alcohol. A blue perchromic acid is extracted into the amyl alcohol layer (Chapter 23):

$$H_2Cr_2O_7 + 4H_2O_2 \rightleftharpoons 2CrO_5 + 5H_2O$$

Aluminium Ion: This ion also gives a white gelatinous precipitate of Al $(OH)_3$ on the addition of NH_4OH even in the presence of NH_4Cl. This is amphoteric and dissolves in excess alkali to form the soluble aluminate.

$$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl$$

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

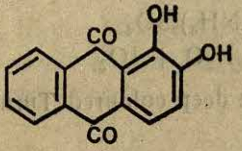


Fig. 28.2. Alizarin

Sodium salt of alizarin (Fig. 28.2) is violet in colour. This sensitive reagent reacts with $NaAlO_2$ in the presence of acetic acid to give a red colour or precipitate of aluminium alizarin:

REACTIONS OF METAL IONS OF GROUP IIIB

Cobalt Ion: The black cobalt sulphide precipitate is obtained from neutral or ammoniacal medium. It is insoluble in dilute acetic acid but dissolves in nitric acid:

$$3CoS + 8HNO_3 \rightarrow 3Co(NO_3)_2 + 2NO + 4H_2O + 3S$$

On addition of ammonium thiocyanate to a solution of cobalt (II) a blue coloured solution of tetrathiocyanato complex is formed. This can be extracted by ether or amyl alcohol:

$$CoCl_2 + 4NH_4NCS \rightarrow (NH_4)_2[Co(NCS)_4] + 2NH_4Cl$$

Potassium cyanide first precipitates brown $Co(CN)_2$ which dissolves in excess KCN on heating to give yellow cobalticyanide:

$$Co(CN)_2 + 4KCN \rightarrow K_4[Co\ (CN)_6]$$

$$4K_4[Co(CN)_6] + 2H_2O + O_2 \rightarrow 4K_3[Co(CN)_6] + 4KOH$$

Such a reaction brings little change with nickel (II). Hence this is a good test for cobalt in the presence of nickel.

Nickel Ion: With H_2S in ammoniacal medium black NiS is precipitated. This precipitate is also soluble in concentrated HNO_3:

$$3NiS + 8HNO_3 \rightarrow 3Ni(NO_3)_2 + 2NO + 4H_2O + 3S$$

The most distinctive qualitative and quantitative reaction of nickel (II) is with dimethylglyoxime. In neutral or ammoniacal medium nickel (II) is quantitatively precipitated as bis (dimethylglyoximato) nickel (II) (Chapter 6; Fig. 6.3). The reaction is so sensitive that one part nickel in as much as three lac parts solution will produce a perceptible rose-red colour. In larger concentration there appears a beautiful rose-red precipitate.

Manganese Ion: Brown coloured MnS is precipitated by H_2S in ammoniacal medium. Manganese is sometimes carried as a hydroxide in group IIIA which is oxidised in air to MnO_2. The oxidation is hastened by H_2O_2:

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O$$

Manganese (II) can be easily oxidised to beautiful purple permanganate by oxidation with sodium bismuthate in the presence of H_2SO_4 or HNO_3:

$$2MnSO_4 + 5NaBiO_3 + 16HNO_3 \rightarrow 2HMnO_4 + 5Bi(NO_3)_3 + NaNO_3 + 2Na_2SO_4 + 7H_2O$$

Lead dioxide can also force this oxidation:

$$2MnSO_4 + 5PbO_2 + 6HNO_3 \rightarrow 2HMnO_4 + 3Pb(NO_3)_2 + 2PbSO_4 + 2H_2O$$

Zinc Ion: ZnS is precipitated as a white precipitate from an ammoniacal medium by the passage of H_2S. This ion reacts with ammonia to precipitate $Zn(OH)_2$ which dissolves readily in excess NaOH:

$$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$$

With potassium ferrocyanide sparingly soluble potassium zinc ferrocyanide is formed:

$$6ZnSO_4 + 4K_4[Fe(CN)_6] \rightarrow 2Zn_3K_2[Fe(CN)_6]_2 + 6K_2SO_4$$

Addition of excess NH_4NCS to cobalt ion gives deep blue $[Co(NCS)_4]^{2-}$. Addition of mercuric ion gives deep blue precipitate of $Hg[Co(NCS)_4]$, a good test for cobalt.

$$CoCl_2 + 4NH_4NCS \rightarrow (NH_4)_2[Co(NCS)_4] + 2NH_4Cl$$

$$HgCl_2 + (NH_4)_2(Co(NCS)_4) \rightarrow Hg[Co(NCS)_4] + 2NH_4Cl$$

Zinc ion may also be tested by a modification of the above reactions. Mercuric ion is first treated with excess of thiocyanate to give $(Hg(SCN)_4)^{2-}$. To this solution first zinc ion and then a few drops of very dilute (0.02%) solution of $CoSO_4$ is added. A blue precipitate of mixed crystals of $Zn[Hg(SCN)_4]$ and $Co[Hg(SCN)_4]$ is formed.

Tables 28.11 and 28.12 give the separation methods for the ions of groups IIIA and IIIB. Presence of phosphate and borate may interfere with the subsequent analyses. Borate may be removed by repeated evaporation with HCl. If present phosphate has to be removed by the basic acetate method or by the zirconium nitrate method.

Table 28.11. Analysis of Group IIIA

The filtrate from group II(A and B) precipitates is boiled to remove the H_2S. A few drops of HNO_3 are added and the solution warmed. The mixture is now tested for the presence or absence of iron and phosphate. If phosphate is present it is removed by the basic acetate method or the zirconium nitrate method. NH_4Cl is now added and the solution made ammoniacal. In the absence of phosphate the solution is treated directly with NH_4Cl and NH_4OH and the analyses carried out as indicated below. The precipitates of $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$ and little $Mn(OH)_2$ ($\sim MnO_2$) are filtered and the filtrate reserved for analysis of group IIIB. The hydroxide precipitates are taken in a beaker and heated with Na_2O_2 (or H_2O_2 plus NaOH). The mixture is filtered again.

Table 28.11. (Continued)

Residue: May contain $Fe(OH)_3$ alongwith little MnO_2. The residue is dissolved in 1:1 HNO_3 and divided in two parts: 1. One part is diluted with water and treated with $K_4Fe(CN)_6$. A deep Prussian blue precipitate indicates the presence of iron. 2. The other part is treated with sodium bismuthate. A fine violet colour develops if manganese is present.	*Filtrate*: May contain yellow Na_2CrO_4 and colourless $NaAlO_2$. If no yellow colour develops then chromium is absent. If the solution is yellow it is divided in two parts: 1. One part is made acidic with dilute HNO_3 and cooled. Amyl alcohol and H_2O_2 are added and shaken. If chromium is present the amyl alcohol layer turns blue. 2. To the other part solid NH_4Cl is added. If aluminium is present white gelatinous precipitate of $Al(OH)_3$ is formed. The precipitate is tested with alizarin. If the violet colour of alizarin changes to a red colour or precipitate aluminium is indicated.

28.7. REACTIONS OF METAL IONS OF GROUP IV

This qualitative group consists of the three alkaline earths, namely calcium, strontium and barium. Sulphides, chlorides and hydroxides of these metal ions are all soluble. Hence they have remained outside the range of the previous three groups. Among the insoluble salts of these metal ions are the carbonates, sulphates and the chromates—the solubility varying from one member to another.

The group reagent is carbonate. All the three carbonates are insoluble in ammoniacal medium. However all the carbonates are soluble in acetic and other acids. Sulphates are sparingly soluble. In particular barium sulphate is insoluble in presence of even dilute HCl and hence this is made use of in the gravimetric estimation of barium. Barium chromate is also quite insoluble to allow gravimetric estimation.

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$$

$$BaCl_2 + K_2CrO_4 \rightarrow BaCrO_4 + 2KCl$$

Strontium chromate is insoluble in water but soluble even in acetic acid and this makes a significant difference with barium.

The oxalates are insoluble in water but those of strontium and barium are soluble in warm acetic acid. But calcium oxalate is fairly insoluble:

$$CaCl_2 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4 + 2NH_4Cl$$

The filtrate from groups (IIIA and IIIB) contains excess ammonia and sulphide ion. Exposure to air sometimes leads to the oxidation of the sulphide to sulphate. In order to obviate any bad effect the filtrate is first treated with acetic acid and taken almost to dryness. A few millilitre of concentrated HNO_3 are

Table 28.12. Analysis of Group IIIB

After filtering off the precipitates of the group IIIA hydroxides the filtrate is treated with H_2S. Now the group IIIB sulphides, namely CoS, NiS, MnS and ZnS, are precipitated. These precipitates are filtered and washed with a solution of NH_4Cl. The filtrate is reserved for analysis of group IV metal ions. The group IIIB sulphides are taken in a small beaker and stirred with dilute HCl. MnS and ZnS dissolve out but not CoS and NiS. The mixture is filtered.

<table>
<tr>
<td rowspan="2">*Residue*: May be CoS and NiS. Borax bead test is performed with a little of this residue. A blue coloured bead indicates cobalt. If nickel alone is present a brown coloured bead is obtained.
The residue is dissolved in concentrated HNO_3 and the excess acid removed by taking the mass to dryness. The solid is dissolved in water and the solution divided in two parts:
1. In the first part NH_4Cl, NH_4OH and dimethylglyoxime is added. A beautiful rose-red precipitate indicates nickel.
2. In the second part NH_4NCS is added and then shaken with amyl alcohol. In the presence of cobalt the amyl alcohol layer is coloured blue.</td>
<td colspan="2">*Filtrate*: May contain $MnCl_2$ and $ZnCl_2$. The solution is boiled to drive off H_2S. After cooling excess NaOH is added. and filtered.</td>
</tr>
<tr>
<td>*Residue*: May be $Mn(OH)_2$ or MnO_2. The residue is treated with sodium bismuthate in presence of HNO_3 or H_2SO_4. A fine purple colour develops in the presence of manganese.</td>
<td>*Filtrate*: May have Na_2ZnO_2. The solution is divided in two parts:
1. Acidified with dilute acetic acid and then treated with H_2S. A white precipitate of ZnS indicates zinc.
2. In presence of dilute acetic acid addition of $(NH_4)_2$ $Hg(SCN)_4$ plus little $CoSO_4$ solution gives a blue precipitate. Presence of zinc is indicated.</td>
</tr>
</table>

added and again taken to dryness. The ammonium salts are then strongly heated to remove any undesirable anions. Now NH_4Cl and NH_4OH are added and the solution containing the alkaline earths and the remaining group V members is thus made ammoniacal. The group reagent $(NH_4)_2CO_3$ is added in the form of a saturated solution. Calcium, strontium and barium are precipitated as carbonates. These are filtered and analysed following the directions given in Table 28.13.

Table 28.13. Analysis of Group IV

The precipitate obtained on the addition of ammonium carbonate to the ammoniacal solution of the fitrate from group IIIB, as directed above, contains $CaCO_3$, $SrCO_3$ and $BaCO_3$. The precipitate is dissolved out by hot 2*N* acetic acid. A small portion of the solution is treated with K_2CrO_4. If a precipitate of $BaCrO_4$ appears then the entire solution is treated with K_2CrO_4. The mixture is boiled for a while and filtered.

<table>
<tr>
<td rowspan="2"><i>Residue</i>: Yellow coloured precipitate indicates barium. The precipitate gives an apple green colour in the Bunsen flame.</td>
<td colspan="2"><i>Filtrate</i>: May contain strontium and calcium. About 1 ml of NH_4OH and excess $(NH_4)_2CO_3$ are added to precipitate both the ions as carbonates. The precipitate is boiled with 2<i>N</i> acetic acid to remove all CO_2. The solution is cooled and treated with 4-5 ml. of $(NH_4)_2SO_4$. Thereafter the mixture is again filtered.</td>
</tr>
<tr>
<td><i>Residue</i>: White residue indicates $SrSO_4$. Gives a crimson red colour in the Bunsen flame.</td>
<td><i>Filtrate</i>: May contain calcium. The solution is heated with a strong solution of $(NH_4)_2C_2O_4$. White precipitate indicates calcium. Gives a brick-red colour to the Bunsen flame.</td>
</tr>
</table>

28.8. REACTIONS OF METAL IONS OF GROUP V

This group contains magnesium, sodium, potassium ions. *Magnesium Ion*: This ion is precipitated as $Mg(NH_4)PO_4.6H_2O$ on the addition of Na_2HPO_4 to a magnesium solution in the presence of NH_4Cl and NH_4OH. The crystalline precipitate appears rather slowly. Scratching the sides of the container helps the precipitate to appear early. 8-Hydroxyquinoline ligand precipitates magnesium as bis (8-hydroxyquinolinato) magnesium (II) from ammoniacal medium as a yellow precipitate. This is also one of the compounds which is utilised in the gravimetric estimation of magnesium.

Sodium Ion: Almost all its salts are soluble. However a yellow precipitate of sodium zinc uranyl acetate nonahydrate, $NaZn(UO_2)_3(CH_3COO)_9.9H_2O$ is obtained on the addition of zinc uranyl acetate, $Zn(UO_2)_2(CH_3COO)_6$. This test has to be performed after removing all the other metal ions which might otherwise react with zinc uranyl acetate.

Potassium Ion: Sodium cobaltinitrite gives a yellow precipitate with potassium ion:

$$Na_3[Co(NO_2)_6] + 2KCl \rightarrow K_2Na[Co(NO_2)_6] \downarrow + 2NaCl$$

Sodium perchlorate reacts with potassium ion to precipitate sparingly soluble potassium perchlorate:

$$NaClO_4 + KCl \rightarrow KClO_4 \downarrow + NaCl$$

Table 28.14 describes the separation of the group V ions.

Table 28.14. Analysis of Group V

The filtrate from group IV may contain the ions of group V. The filtrate contains substantial amount of ammonium ion, many of whose reactions are similar to those of potassium ion. Therefore the filtrate of group IV is taken in a porcelain dish and evaporated to dryness and then further heated to destroy all ammonium salts. If any solid white residue is left it may contain the group V ions. The residue is dissolved in small amount of water and the solution divided in three parts.

1. To one portion NH_4Cl, NH_4OH and then Na_2HPO_4 are added and the sides of the test tube scratched. If magnesium is present a white crystalline precipitate, $Mg(NH_4)PO_4.6H_2O$, appears.	2. To the second portion zinc uranyl acetate is added. In the presence of sodium ion a yellow precipitate of sodium zinc uranyl acetate is formed. A golden yellow colour appears in the Bunsen flame.	3. To the third portion sodium cobaltinitrite is added alongwith with a drop or two of acetic acid. In the presence of potassium a yellow precipitate of potassium sodium cobaltinitrite appears.

28.9. REACTIONS OF ANIONS

Borate Ion: The borate salt is taken in a dry test tube and mixed with about 2 ml. concentrated H_2SO_4 and 5 ml. methyl alcohol. The mixture is carefully heated and the issuing gas is lighted at the mouth of the test tube. A green flame indicates borate ion. In the case of free boric acid sulphuric acid is not necessary in the above test. Thus free boric acid and a borate salt can be distinguished:

$$Na_2B_4O_7 + H_2SO_4 \rightarrow H_2B_4O_7 + Na_2SO_4$$

$$H_2B_4O_7 + 5H_2O \rightarrow 4H_3BO_3$$

$$H_3BO_3 + 3CH_3OH \rightarrow \underset{\text{(methyl borate)}}{B(OCH_3)_3} \uparrow + 3H_2O$$

Silicate Ion: About 0.2 gram of a silicate salt is taken in a lead crucible and this is mixed with about 0.1 gram of CaF_2 and a few drops of concentrated H_2SO_4. The crucible is now covered with a lead lid provided with a small opening. The crucible is heated on an asbestos board over a low flame. SiF_4 gas comes out through the opening. A water drop on a platinum loop is held over the issuing gas. SiF_4 is hydrolysed to cloudy silicic acid:

$$SiO_2 + 2CaF_2 + 2H_2SO_4 \rightarrow 2CaSO_4 + SiF_4 \uparrow + 2H_2O$$

$$3SiF_4 + 4H_2O \rightarrow H_4SiO_4 \downarrow + 2H_2SiF_6$$

Fluoride Ion: The fluoride salt is taken in a dry test tube and is mixed with a little SiO_2 and a few drops of concentrated H_2SO_4. The test tube is carefully heated and a drop of water at the end of a glass rod is held over the mouth of the tube. The water drop turns turbid due to the formation of silicic acid:

$$2KF + H_2SO_4 \rightarrow 2HF + K_2SO_4$$
$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$
$$3SiF_4 + 4H_2O \rightarrow H_4SiO_4 \downarrow + 2H_2SiF_6$$

Thus the tests of silicate and fluoride ions are complementary to each other.

Chloride Ion: When a chloride salt is heated with MnO_2 and concentrated H_2SO_4 there evolves a greenish yellow gas (chlorine). It has a pungent smell and turns potassium-iodide starch paper violet:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$
$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

Chromyl chloride test is also a distinctive test of chloride ion. A mixture of the chloride salt and some $K_2Cr_2O_7$ is taken in a hard glass test tube provided with a delivery tube. A few ml. of concentrated H_2SO_4 are added and the mixture carefully heated. Deep red coloured CrO_2Cl_2 gas evolves and is absorbed in NaOH solution. The solution is yellow due to the formation of chromate. It is acidified, preferably with acetic acid, and treated with lead or barium acetate. A yellow precipitate of $PbCrO_4$ or $BaCrO_4$ is obtained.

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 \uparrow + 2KHSO_4 + 4NaHSO_4 + 3H_2O$$
$$CrO_2Cl_2 + 4NaOH \rightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$

Silver ion reacts with chloride ion in the presence of dilute HNO_3 to give a white precipitate of AgCl which is soluble in ammonia:

$$NaCl + AgNO_3 \rightarrow AgCl \downarrow + NaNO_3$$
$$AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$$

Bromide Ion: On heating a bromide salt with concentrated H_2SO_4 first HBr is formed, which undergoes oxidation to red bromine vapour:

$$NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$$
$$2HBr + H_2SO_4 \rightarrow Br_2 \uparrow + SO_2 + 2H_2O$$

Bromide ion is also oxidised by MnO_2 and H_2SO_4 to bromine:

$$2NaBr + MnO_2 + 3H_2SO_4 \rightarrow Br_2 \uparrow + 2NaHSO_4 + MnSO_4 + 2H_2O$$

Since chlorine is a stronger oxidant than bromine it is a common experience to observe liberation of bromine when a bromide salt is shaken with chlorine water:

$$2KBr + Cl_2 \rightarrow Br_2 + 2KCl$$

Silver nitrate precipitates bromide ion as silver bromide. This is soluble in large excess of ammonia:

$$AgBr + 2NH_4OH \rightarrow [Ag(NH_3)_2]Br + 2H_2O$$

Iodide Ion: This is readily oxidised by hot concentrated H_2SO_4 to violet vapours of iodine. Similar oxidation occurs also in the presence of MnO_2 and H_2SO_4.

Chlorine water also liberates iodine from iodide salts. With silver nitrate yellow AgI is precipitated but this is not soluble in NH_4OH.

Analysis of a mixture of chloride, bromide and iodide: If the mixture is water insoluble it is common practice to prepare a sodium carbonate extract by boiling the mixture with aqueous Na_2CO_3 and then filtering off the insoluble carbonates. The filtrate obviously contains now a mixture of the three halides as their sodium salts. A part of this solution is made acidic with HCl and then CCl_4 added and shaken with chlorine water. If iodide is present then it is oxidised to iodine which passes onto the CCl_4 layer. The upper CCl_4 layer assumes a fine pleasing violet colour. Shaking with more of chlorine water will oxidise the free iodine to colourless iodic acid which will now come back to the aqueous layer:

$$I_2 + 5Cl_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$$

If the mixture contains additionally a bromide then on shaking with further chlorine water the CCl_4 layer will now turn red or orange. In case iodine is absent but bromine is present then the CCl_4 will turn red at the first instance on shaking with chlorine water.

In another portion of the sodium carbonate extract enough HNO_3 is added and the solution heated to drive off all the iodine and bromine. Boiling should be avoided as it may expel some of the HCl. Now silver nitrate is added. If chloride is present a white precipitate of AgCl appears, which is soluble in ammonia.

Sulphide Ion: On heating with dilute H_2SO_4 a smell of rotten eggs is given out indicating H_2S. This gas changes the colour of acidified dichromate paper from orange to green due to reduction. Lead acetate paper is turned black due to the formation of black lead acetate:

$$Na_2S + 2H_2SO_4 \rightarrow H_2S + 2NaHSO_4$$

$$\underset{\text{(orange)}}{K_2Cr_2O_4} + 8HCl + 3H_2S \rightarrow 2KCl + \underset{\text{(green)}}{2CrCl_3} + 7H_2O + 3S\downarrow$$

$$Pb(CH_3COO)_2 + H_2S \rightarrow \underset{\text{(black)}}{PbS\downarrow} + 2CH_3COOH$$

Soluble sulphides precipitate black Ag_2S from silver nitrate solution. A soluble sulphide reacts in alkaline medium with sodium nitroprusside to change its red colour to a beautiful violet:

$$Na_2S + \underset{\text{(light red)}}{Na_2\,[Fe(NO)(CN)_5]} \rightarrow \underset{\text{(deep violet)}}{Na_4\,[Fe(NOS)(CN)_5]}$$

Sulphite Ion: Addition of HCl or H_2SO_4 to a sulphite salt gives off colourless suffocating SO_2 gas. This gas also turns the colour of a dichromate paper from yellow to green:

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + SO_2\uparrow + H_2O$$

$$K_2Cr_2O_7 + 3H_2SO_3 + 2HCl \rightarrow 2KCl + Cr_2(SO_4)_3 + 4H_2O$$

Sulphate Ion: The most distinguishing reaction of this ion is with barium chloride whereby a white precipitate of $BaSO_4$, insoluble in HCl, is obtained. Barium ion or the sulphate ion is gravimetrically estimated by way of this precipitate.

The sulphate salt may be mixed with sodium carbonate and charcoal and may be reduced to sulphide by heating on a charcoal block or in a platinum loop by a Bunsen flame. Thereafter the sulphide may be dissolved in water and the sodium nitroprusside test performed to get a characteristic violet colour:

$$K_2SO_4 + 4C \rightarrow K_2S + 4CO$$

$$\underset{\text{(light red)}}{K_2S + Na_2[Fe(NO)(CN)_5]} \rightarrow \underset{\text{(deep violet)}}{K_2Na_2[Fe(NOS)(CN)_5]}$$

Thiosulphate Ion: Heating a thiosulphate salt with acid gives off SO_2 and precipitates sulphur:

$$Na_2S_2O_3 + 2HCl \rightarrow SO_2 \uparrow + S \downarrow + 2NaCl + H_2O$$

Thiosulphate can also discharge the colour of iodine due to reduction:

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O + 2NaI$$

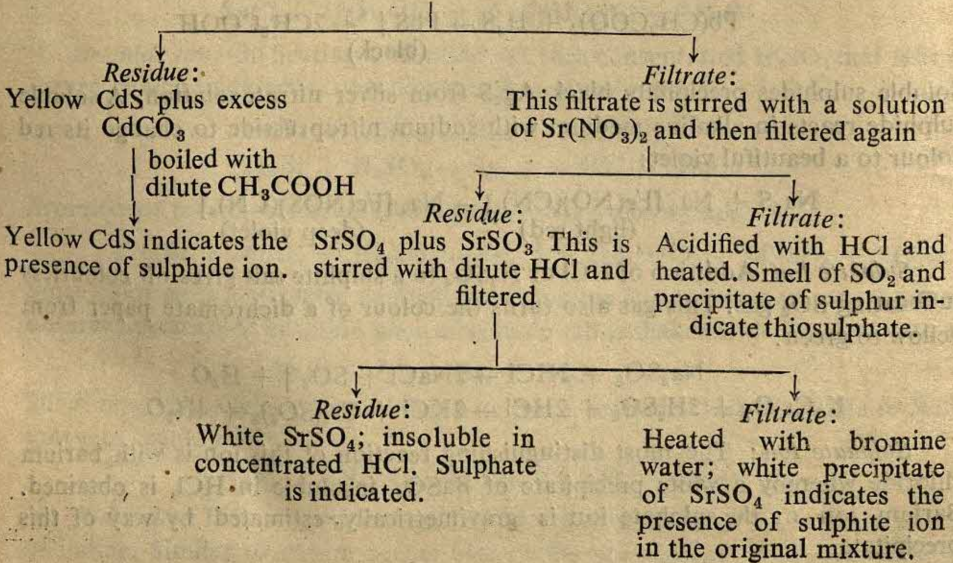
With silver ion a white precipitate of $Ag_2S_2O_3$ is formed. Excess thiosulphate forms a soluble thiosulphato complex (Chapter 25). On heating the silver thiosulphate decomposes to black Ag_2S:

$$Na_2S_2O_3 + 2AgNO_3 \rightarrow Ag_2S_2O_3 \downarrow + 2NaNO_3$$

$$Ag_2S_2O_3 + H_2O \xrightarrow{\text{heat}} Ag_2S \downarrow + H_2SO_4$$

$$Ag_2S_2O_3 + 3Na_2S_2O_3 \longrightarrow 2Na_3[Ag(S_2O_3)_2]$$

Analysis of a mixture of sulphide, sulphite, thiosulphate and sulphate: A sodium carbonate extract is made by boiling a mixture of the above salts with aqueous sodium carbonate. The filtrate from the above reaction contains the sodium salts of the above sulphur acids. The solution is treated with excess of solid $CdCO_3$ and then the mixture filtered:



Residue: Yellow CdS plus excess $CdCO_3$

boiled with dilute CH_3COOH

Yellow CdS indicates the presence of sulphide ion.

Filtrate: This filtrate is stirred with a solution of $Sr(NO_3)_2$ and then filtered again

Residue: $SrSO_4$ plus $SrSO_3$ This is stirred with dilute HCl and filtered

Filtrate: Acidified with HCl and heated. Smell of SO_2 and precipitate of sulphur indicate thiosulphate.

Residue: White $SrSO_4$; insoluble in concentrated HCl. Sulphate is indicated.

Filtrate: Heated with bromine water; white precipitate of $SrSO_4$ indicates the presence of sulphite ion in the original mixture.

Nitrite Ion: Brown NO_2 gas is readily given off on reaction with dilute HCl:

$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

$$2NO + O_2 \rightarrow 2NO_2$$

In the presence of dilute H_2SO_4 or CH_3COOH nitrite ion reacts with KI to give iodine:

$$2KI + 2HNO_2 + 2CH_3COOH \rightarrow I_2 + 2NO + 2CH_3COOK + 2H_2O$$

Nitrites are converted to nitrogen on reacting with urea:

$$CO(NH_2)_2 + 2HNO_2 \rightarrow 2N_2 \uparrow + CO_2 + 3H_2O$$

Brown ring test may be performed under care as directed below. A fresh solution of good quality $FeSO_4$ is acidified with acetic acid. This solution is taken in a test tube and held in an inclined position. A nitrite solution is then added along the side of the inclined test tube so carefully that the solutions do not undergo immediate mixing. In the presence of nitrite there appears a brown ring at the juncture of the two solutions:

$$2NaNO_2 + 2CH_3COOH \rightarrow 2CH_3COONa + 2HNO_2$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

$$FeSO_4 + NO + 5H_2O \rightarrow \underset{\text{(brown ring)}}{[Fe(NO)(H_2O)_5]SO_4}$$

Nitrate Ion: Brown coloured NO_2 gas is liberated on treating a nitrite salt with copper turnings and concentrated H_2SO_4:

$$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_3$$

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

On boiling a solution of a nitrate with aluminium powder and NaOH there occurs evolution of ammonia. If the sample already contains some ammonium salt then it is first boiled with NaOH solution to decompose the entire amount of ammonium salt. Thereafter it is boiled with aluminium powder and NaOH:

$$3NaNO_3 + 5NaOH + 8Al + 2H_2O \rightarrow 3NH_3 + 8NaAlO_2$$

Nitrate also responds—in fact responds better—to brown ring test. In the case of nitrate sulphuric acid has to be used instead of acetic acid. Ba^{2+} and Pb^{2+} interfere due te precipitation of white $BaSO_4$ and $PbSO_4$.

Analysis of a mixture of nitrite and nitrate: Dilute HCl is enough to decompose the nitrite by bringing off NO_2. After the entire NO_2 is given off the solution is heated with concentrated H_2SO_4 and copper powder. Alternatively the nitrite may be decomposed by heating with urea (evolution of nitrogen) and thereafter the solution is boiled with aluminium powder and NaOH. Under this condition nitrate will liberate ammonia.

Phosphate Ion: Magnesia mixture ($MgCl_2 + NH_4Cl + NH_4OH$) gives a crystalline precipitate of magnesium ammonium phosphate:

$$Na_2HPO_4 + MgCl_2 + NH_4OH \rightarrow Mg(NH_4)PO_4 \downarrow + 2NaCl + H_2O$$

The most distinguishing reaction of a phosphate ion is with ammonium molybdate. In the presence of HNO_3 at about 50°C phosphate and ammonium molybdate react to give beautiful yellow precipitate of ammonium phosphomolybdate:

$$Na_2HPO_4 + 12(NH_4)_2MoO_4 + 23HNO_3 \rightarrow (NH_4)_3\,[PMo_{12}O_{40}] \downarrow + 2NaNO_3 + 21NH_4NO_3 + 12H_2O$$

Arsenate (AsO_4^{3-}) ion also produces a similar yellow precipitate with ammonium molybdate but this requires nearly a boiling temperature.

Analysis of a mixture of a phosphate, arsenite and arsenate: A sodium carbonate extract is first prepared. After filtering off the insoluble carbonates the filtrate contains the sodium salts of phosphate, arsenite and arsenate. Addition of magnesia mixture gives a precipitate of $Mg(NH_4)PO_4$ and $Mg(NH_4)AsO_4$. The mixture is then filtered.

Residue:
White precipitate is dissolved in dilute HCl and boiled to remove all SO_2 gas. Then H_2S is passed through the solution and filtered.

Residue:
Yellow precipitate of As_2S_3 indicates arsenate ion.

Filtrate:
Ammonium molybdate test performed. A yellow precipitate indicates phosphate.

Filtrate:
This is acidified with HCl. H_2S is then bubbled through. A yellow precipicipitate indicates arsenite.

Removal of phosphate: The filtrate from group II (A and B) is boiled to get rid of any H_2S. A portion of the solution is tested for phosphate. If phosphate and later group metal ions are present then phosphate has to be removed. If phosphate is not removed then on making the solution ammoniacal the phosphates of most of the later group members will be precipitated (eg. Cr(III), Al(III), Co(II), Ni(II) etc.). There are two methods available for separation of phosphate.

1. *Zirconium nitrate method*: The filtrate from group II is boiled to remove H_2S and the solution treated with two or three drops of HNO_3. The acidity is maintained at about 2*N*. Little ammonium chloride is added being followed by a solution of zirconyl nitrate in dilute HNO_3. The phosphate present is precipitated as zirconyl phosphate $ZrO(H_2PO_4)_2$. After filtration of the zirconyl phosphate (preferably with the aid of little filter paper pulp) the solution contains little zirconyl ion. The excess zirconyl ion will be precipitated in group IIIA along with iron (III) etc. After treatment with Na_2O_2 it will stay with the $Fe(OH)_3$ and will create no problem in the detection of ferric iron. This is a good method of separation of phosphate but is not usually practised because of the high cost of the zirconium compound.

2. *Basic acetate method*: It is the usually practised method. H_2S is removed from the filtrate of the group II by boiling. The solution is then boiled with 1 ml.

of HNO_3, cooled and treated with NH_4Cl and NH_4OH. If a precipitate appears then the solution is cleared with dropwise addition of dilute HCl. A small portion of this solution is next tested for the presence of ferric iron by the addition of ammonium thiocyanate or potassium ferrocyanide. The rest of the solution is made very slightly ammoniacal. Now 5 ml. of glacial acetic acid and 5 ml. of saturated ammonium acetate are added. A neutral solution of $FeCl_3$ in water is added little by little under stirring till the mixture assumes the common tea colour. This is then diluted with 100-150 ml. of water and boiled. The mixture is filtered hot.

Residue: May contain the phosphates of iron (III), aluminium (III) chromium (III) and basic iron acetate. This residue has to be analysed as for group IIIA.	*Filtrate*: The solution is evaporated to a volume of about 30 ml. NH_4Cl and slight excess of NH_4OH are again added. If any precipitate appears it is removed by filtration. The filtrate is now free from phosphate and is ready for analyses of groups IIIB, IV and V.

28.10. ANALYSES OF SOME INSOLUBLE COMPOUNDS

There are some compounds which remain insoluble even in aqua regia. These are termed as insoluble salts. The following are some common insoluble salts:

I. *Silver halides*: AgCl(white); AgBr (light yellow); AgI (yellow);

II. *Metal Sulphates*: $PbSO_4$ (white); $BaSO_4$ (white); $SrSO_4$ (white);

III. *Ignited oxides*: Al_2O_3 (white); SnO_2 (white); Fe_2O_3 (red-brown); Cr_2O_3 (green);

IV. *Ignited chromate*: $PbCrO_4$ (brown)

V. *Silica*: It may be present as such in the sample or may result from some silicate in the sample mixture on acid treatment.

Procedure: If the insoluble material is white it may be any one of $PbSO_4$, $BaSO_4$, $SrSO_4$, Al_2O_3, SnO_2, CaF_2 and SiO_2.

$BaSO_4$ and $SrSO_4$: A little of the sample is taken in a platinum loop and heated in the reducing zone of the Bunsen flame. This will convert the sulphates into the sulphides. The platinum along with the sulphides is moistened with HCl and held at the outer zone of the Bunsen flame. A crimson red flame and an apple green flame indicate strontium and barium respectively..

CaF_2: Flame test gives a transient brick-red colour.

$PbSO_4$: It is soluble in a hot concentrated solution of ammonium acetate.

After filtration from any insoluble material the filtrate is tested for lead (II) and sulphate ions. Lead (II) can be detected with H_2S when a black precipitate of PbS is formed. Chromate will give a yellow precipitate of lead chromate. Sulphate ion can be tested with barium chloride in the presence of HCl.

The other insoluble materials are boiled with NaOH solution and filtered. The filtrate may contain Na_2CrO_4 (yellow), colourless $NaAlO_2$, Na_2SiO_3, NaF,

Na_2SnO_3, $NaSbO_3$, Na_2SO_4. The solution has to be divided into several fractions. If the solution looks yellow it may be chromate. Perchromic acid test may be performed and chromium confirmed. Presence of sulphate may be detected via addition of $BaCl_2$ when insoluble $BaSO_4$ is precipitated in HCl medium. Presence of tin (IV) and antimony (III) may be detected by the passage of H_2S in acidic medium. For silicate the solution has to be taken to dryness. The residue has to be mixed with CaF_2 and H_2SO_4 in a lead crucible and the usual test of silicate has to be performed.

EXERCISES

1. Give an account of how solubility product and common ion principle have influenced developing the qualitative scheme of analysis.

2. Why is it necessary to remove phosphate ion before passing from group II to the later groups?

3. Name a few compounds which are insoluble in aqua regia. How would you proceed to detect such compounds?

4. Give a few distinguishing reactions of mercuric mercury and mercurous mercury.

5. Explain why ammonium chloride is added before going to group III.

6. Describe the methods of detection of the following anions present in a mixture : (*a*) chloride, bromide and iodide (*b*) sulphide and sulphate (*c*) nitrite and nitrate.

7. Write notes on :
(*a*) Nessler's reagent, (*b*) Chromyl chloride test, (*c*) Yellow ammonium sulphide.

8. Describe the uses of borax and molybdate in qualitative tests.

9. How would you distinguish between an arsenite and arsenate?

10. How would you proceed to identify copper (II) and cadmium (II) in a mixture?

CHAPTER 29

QUANTITATIVE ANALYSIS

29.1. INTRODUCTION

In these days of astounding scientific achievements chemists have in their armoury a very large number of instrumental techniques for the quantitative estimation of metal ions and anions. In this elementary level text we can devote only to two time-honoured classical techniques with which college level students need to get them familiar. In simplest terms these are:

I. Volumetric Analysis II. Gravimetric Analysis

Volumetric analysis of a metal ion or an anion essentially is the determination of the volume of a *standard solution* which is found to react quantitatively with the solution of the ion under analysis. The amount of the ion is then calculated from the knowledge of the volume and the strength of the standard solution. Volumetric determination involves titrating the solution under analysis with a standard solution of a known reagent. Hence volumetric analyses are also referred to as titrimetric analyses.

Gravimetric analysis of a metal ion or an anion involves precipitating the ion concerned with the aid of a suitable reagent as an insoluble compound and weighing the precipitate. The amount of the substance under analysis is determined from a knowledge of the weight of the precipitate and its formula.

We discuss below the analyses of some very common ions which we often come across in the chemical laboratory.

29.2. IRON

This metal is determined in the laboratory both by volumetric and gravimetric procedures. Volumetric procedure may involve either of the two standard oxidants: potassium dichromate or potassium permanganate. Of these two, potassium dichromate serves as a *primary standard* i.e. its strength is obtained directly from its weight used in preparing the standard solution. This is due to the fact that this substance is obtained in a very pure condition and its aqueous solution is very stable. On the other hand potassium permanganate is not obtained very pure and its aqueous solution is also not very stable on standing. Hence its strength is determined by titration against another primary standard. Because of this deficiency potassium permanganate is a *secondary standard*.

The commonest gravimetric procedure adopted for iron is to take iron to the ferric state and precipitate the iron as ferric hydroxide. After filtering off the precipitate it is washed, ignited to the oxide Fe_2O_3 and weighed.

29.2.1. Potassium dichromate method: As we have mentioned earlier this reagent serves as a primary standard. During reaction with ferrous iron hexavalent chromium of $K_2Cr_2O_7$ is reduced to trivalent chromium. Taking into account that one molecule of the dichromate contains as many as two hexavalent chromium there will be a total of six unit reduction per mole of the dichromate. Thus a *normal solution* (which contains one equivalent per litre of the solution) of potassium dichromate contains one-sixth the gram molecular weight of $K_2Cr_2O_7$ per litre i.e. 294.22/6 = 49.04 gram per litre.

Therefore 1000 ml ($N/10$) dichromate = 4.904 gram $K_2Cr_2O_7$

Although potassium dichromate is an excellent primary standard it has a great disadvantage. Its colour is so very light that it cannot serve as its own indicator to indicate the end point of the titration. We have therefore got to use one other reagent which will react with the dichromate at the right moment to bring about some spectacular colour change to indicate the end point. This additional indicator is diphenylamine.

Usually we get iron in the ferric state. This ferric ion is reduced with stannous chloride in $6N$ HCl at about 60°C. As soon as the yellow colour of the ferric iron changes to green or very nearly colourless (depending on the amount of iron) addition of $SnCl_2$ is stopped. In such reduction $SnCl_2$ is always present in some slight excess. The excess $SnCl_2$ has to be removed by the addition of $HgCl_2$ in the cold, whereby a colourless silky precipitate of Hg_2Cl_2 appears:

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 \downarrow + SnCl_4$$

If too much $SnCl_2$ is used during the reduction of ferric to ferrous there appears a black precipitate of mercury, which will mar the titration

$$Hg_2Cl_2 + SnCl_2 \rightarrow Hg\ (\text{black}) \downarrow + SnCl_4$$

Presence of chloride ion is not harmful for dichromate because from an inspection of the standard oxidation reduction potentials it is evident that dichromate cannot oxidise chloride to chlorine (in other words chlorine is a slightly stronger oxidant than dichromate):

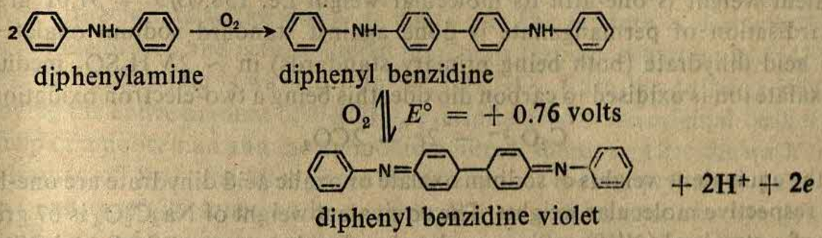
$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O \quad ; E^\circ = +1.33 \text{ volts}$$

$$Cl_2 + 2e \rightleftharpoons 2Cl^- \quad ; E^\circ = +1.36 \text{ volts}$$

$$Fe^{3+} + e \rightleftharpoons Fe^{2+} \quad ; E^\circ = +0.77 \text{ volts}$$

The question now arises how would we know the end point. As we have said earlier this is achieved with the help of a reagent called diphenylamine.

Diphenylamine is a well known oxidation-reduction (redox) indicator. Its solution in H_2SO_4 is oxidised in air to colourless diphenylbenzidine. This latter one is stable in air but can be oxidised by suitable oxidants to diphenylbenzidine violet. The E° of the diphenylbenzidine violet/diphenyl benzidine is $E^\circ = +0.76$ volts. The E° of the Fe^{3+}/Fe^{2+} couple is $E^\circ = +0.77$ volts. It is immediately apparent that dichromate will simultaneously oxidise the ferrous and the diphenylbenzidine. In order that we can dependably utilise diphenylamine as the indicator in the titration of ferrous with dichromate we must see how we can further reduce the E° of the ferric-ferrous couple i.e. we have to make ferrous a better reducing agent so that dichromate will oxidise ferrous in preference to the diphenylbenzidine. Before the titration is started phosphoric acid is added to the solution, which reacts with Fe^{3+} to form $Fe(HPO_4)^+$. This results in the lowering of the E° value because the available concentration of ferric ion is now less. Moreover $Fe(HPO_4)^+$ is colourless, which makes the end point still easier to visualise. Thus the final situation is this: as the solution containing the ferrous ion, phosphoric acid and diphenylamine is titrated by potassium dichromate the oxidant starts oxidising ferrous to ferric which is being complexed by phosphoric acid. As long as there remains any ferrous iron dichromate continues to oxidise ferrous to ferric. After all the ferrous has been oxidised one or two drops of dichromate will immediately oxidise benzidine to the benzidine violet. The beautiful and intense violet colour of the diphenylamine benzidine violet indicates the end point of the titration:



Actual Procedure : The iron solution is treated with a few drops of HNO_3 and the solution boiled to oxidise any ferrous to ferric state. The ferric solution is next treated with NH_4Cl and NH_4OH to precipitate $Fe(OH)_3$. This precipitate is filtered through 41 paper and washed with a solution of NH_4NO_3 to remove adhering materials and also to obviate turning of $Fe(OH)_3$ to the colloidal state. The precipitate is dissolved in hot $6N$ HCl and treated with stannous chloride dropwise at about 60°C. As the yellow colour of the ferric lightens a dilute stannous chloride solution is used for the final stage of the reduction. As soon as the yellow tinge disappears addition of stannous chloride is stopped. The solution is immediately cooled under a running tap. After the solution comes to the room temperature 10 ml of (almost saturated) $HgCl_2$ is added all at a time along the side of the conical flask. If too much $SnCl_2$ has not been added then a colourless fine silky precipitate will only appear. Now about 200 ml 2.5% ($\sim 1N$) H_2SO_4 and 5 ml of syrupy phosphoric acid are added. 10–12 drops of diphenylamine indicator are added and the solution titrated against a standard dichromate solution till there appears fine violet colour. The volume of the dichromate solution is noted and the amount of iron calculated from the following knowledge.

$$1 \text{ ml } (N/10)\ K_2Cr_2O_7 \text{ solution} \equiv 0.005585 \text{ gram iron :}$$

$$\text{Amount of iron} = \text{volume} \times \text{strength of } K_2Cr_2O_7 \text{ (in } N/10) \times 0.005585 \text{ gram.}$$

29.2.2. Potassium permanganate method: It is a strong oxidant and is coloured intense purple. Its advantage is that we do not need any other substance to serve as indicator in titrations involving permanganate. Its colour is so very intesnse that a drop or two of $N/10$ solution is more than enough to impart a visible light purple colour to a volume of about 200-300 ml. But its disadvantage is that it is not obtained as pure as the potassium dichromate nor is its solution stable to standing. Hence it cannot be used as a primary standard. However it can be standardised against standard oxalic acid or sodium oxalate and can be used with confidence as a secondary standard. Its titration in HCl medium is also hazardous. Permanganate being a stronger oxidant than chlorine, is good enough to liberate chlorine from chloride. This chlorine is likely to oxidise, in turn, ferrous to ferric but there is a risk that some chlorine may also escape because of its poor solubility in aqueous medium.

Permanganate has manganese in the oxidation state + 7. During redox reactions in acid medium it is reduced to + 2 manganese. Thus there occurs a five-electron reduction from permanganate to bivalent manganese. Therefore its equivalent weight is one-fifth its molecular weight i.e. 158.03/5 = 31.61 gram. Standardisation of permanganate is done against standard sodium oxalate or oxalic acid dihydrate (both being primary standards) in $\sim 2N$ H_2SO_4 medium. The oxalate ion is oxidised to carbon dioxide, this being a two-electron oxidation:

$$C_2O_4^{2-} - 2e \rightarrow 2CO_2$$

Thus the equivalent weights of sodium oxalate or oxalic acid dihydrate are one-half of the respective molecular weights. The equivalent weight of $Na_2C_2O_4$ is 67 gram. 25 ml of a standard ($N/10$) sodium oxalate is taken in a conical flask and diluted with 150 ml of $2N$ H_2SO_4. The solution is heated to about 70°C and is titrated with permanganate from a burette. The reaction is quite slow to begin with but is quite fast after a few drops of permanganate have been added. The end point is marked by a light purple colour persisting in solution for about 30 seconds. The volume of the permanganate solution is noted and the strength calculated:

$$25 \text{ ml of } y\ (N/10)\ Na_2C_2O_4 \equiv x \text{ ml. permanganate}$$

$$\text{The strength of permanganate} = (25 \times y)/x\ (N/10)$$

Now let us see how we can remove the odd effect of the chloride ion which is likely to be present in the iron solution. The standard redox potentials are:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O;\ E^\circ = +1.52 \text{ volts}$$

$$Cl_2 + 2e \rightleftharpoons 2Cl^-;\ E^\circ = +1.36 \text{ volts}$$

We have to set conditions such that permanganate becomes a weaker oxidant and cannot oxidise chloride ion to chlorine. According to Nernst equation the E° can be reduced if we can increase the concentration of the reductant i.e. the manganese (II) ion in the system (Chapter 7). This is achieved by the use of Zimmermann-Reinhardt solution which contains 70 gram $MnSO_4.4H_2O$, 130 ml concentrated H_2SO_4, 130 ml of syrupy phosphoric acid per litre of the solution. Presence of phosphoric acid leads to the formation of Fe $(HPO_4)^+$, which also helps in reducing the E° of the Fe^{3+}/Fe^{2+} couple. Thus effectively Zimmermann-Reinhardt solution makes permanganate a weaker oxidant but ferrous iron a better reductant. Besides some Mn^{2+} is oxidised to Mn^{2+}, which also helps in the reduction of the $E°$. This does not vitiate the redox procedure because Mn^{3+} can also effectively oxidise ferrous to ferric.

Actual procedure: Iron is reduced as described earlier. Excess $SnCl_2$ is removed by the addition of $HgCl_2$. The solution is diluted with 200 ml water and 25 ml of Zimmermann-Reinhardt solution added. The solution is now titrated with a standard solution of $KMnO_4$ till there is a light purple colour persisting throughout the solution for about 30 seconds.

$$1 \text{ ml } (N/10)\ KMnO_4 \equiv 0.005585 \text{ gram iron}$$

29.2.3. Gravimetric method: The given iron solution is boiled with a few drops of HNO_3 to convert any ferrous iron to the ferric state. The hot solution is then diluted with 200 ml of water. About 3-4 gram of NH_4Cl are added being followed by dropwise addition of 1 : 1 NH_4OH. As the solution becomes ammoniacal the $Fe(OH)_3$ precipitate settles down or floats up. The mixture is carefully boiled for a minute or two and is then filtered preferably through Whatman No. 41 filter paper. The precipitate is washed with 2% NH_4NO_3. Care has to be exercised in removing the entire amount of $Fe(OH)_3$ precipitate from the original beaker with the help of a policeman and the ammonium nitrate solution. After the wash liquid has drained off from the filter paper the filter paper is carefully taken out of the funnel and carefully squeezed into a porcelain or a silica crucible. The crucible has to be ignited to constant weight prior to use in the estimation. A low Bunsen flame has to be used till the filter paper gets dry. Temperature is gradually raised till charring of the filter paper and subsequent oxidation to carbon dioxide is complete. Care should be exercised so that the filter paper does not catch fire. Finally the crucible is heated strongly to a temperature of about 800°C. The crucible is then transferred to a desiccator and cooled for 45-60 minutes and weighed. The difference between the initial and final weights gives the amount of Fe_2O_3. This weight is multiplied by the gravimetric factor of iron in Fe_2O_3 which is 0.6994.

$$\text{Amount of iron} = \text{weight of } Fe_2O_3 \times 0.6994$$

The gravimetric factor for a metal or anion in some precipitate indicates the amount of that metal or anion in 1 *gram of the precipitate.* The gravimetric factor of Fe_2O_3 is 0.6994. This means that in 1 gram of the oxide the amount of iron is 0.6994 gram.

29.3. CALCIUM

29.3.1. Volumetric method: The volumetric method is based on the fact that calcium can be quantitatively precipitated as calcium oxalate in ammoniacal medium. This precipitate is collected, washed free of excess oxalate and then the compound is decomposed by excess of $2N$ H_2SO_4. The liberated oxalic acid is titrated against a standard permanganate solution and the calcium calculaetd from a knowledge of the volume and the strength of the permanganate solution. The following reactions take place:

$$CaCl_2 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4\downarrow + 2NH_4Cl$$

$$CaC_2O_4 + H_2SO_4 \rightarrow H_2C_2O_4 + CaSO_4$$

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + \uparrow 10CO_2 + 8H_2O$$

Actual procedure: An aliquot of the given calcium solution is taken in a beaker. A few ml. of dilute HCl and 200 ml water are now added being followed by a few drops of methyl red indicator. The solution is warmed to about 70°C and 25 ml. of 6% ammonium oxalate solution added. 1 : 1 NH_4OH is added drop by drop till the indicator changes its red acid colour to the yellow alkaline colour. The precipitated calcium oxalate is kept warm for about an hour and then filtered through a Whatman No. 42 filter paper. The beaker and the precipitate are washed several times to get the precipitate free from excess oxalate. Washing is done with cold water. The precipitate is dissolved and washed out into a conical flask with the aid of 150-200 ml of $2N$ H_2SO_4. The solution is brought to a temperature of about 70°C and then titrated with $(N/10)$ potassium permanganate to the first light purple colour persisting throughout the entire solution for about 30 seconds.

Note from the reactions shown above that each $C_2O_4^{2-}$ ion is associated with a Ca^{2+} ion i.e. 1000 ml. of N $C_2O_4^{2-} \equiv 40.08/2 \equiv 20.04$ gram of calcium. (Equivalent weight of oxalic acid is half the molecular weight).

Therefore 1000 ml N $KMnO_4 \equiv$ 1000 ml. of N $C_2O_4^{2-} \equiv$ 20.04 gram calcium

$$1\text{ml. of } (N/10)\ KMnO_4 = 0.002004 \text{ gram calcium}$$

29.3.2. Gravimetric method: The calcium ion present in an aliquot of the given solution is treated with 6% ammonium oxalate as directed above. Calcium oxalate is precipitated quantitatively in slightly ammoniacal medium. The precipitate is collected in a No. 42 filter paper and washed as directed above. (The washing here is not quite crucial as any excess ammonium oxalate will undergo decomposition on strong heating). The filter paper is transferred to a previously cleaned and weighed silica crucible and heated on a Bunsen flame. Temperature should be carefully regulated till the entire filter paper is burnt and oxidised. Finally the crucible is heated strongly to a temperature upto about 1000°C to get calcium oxide:

$$CaC_2O_4 \rightarrow CaO + CO\uparrow + CO_2\uparrow$$

The crucible is then cooled in a desiccator and weighed. The weight of the calcium oxide is known from the difference of the two weights of the crucible.

$$\begin{aligned}\text{Amount of calcium} &= \text{weight of calcium oxide} \times \text{gravimetric factor of calcium in calcium oxide}\\ &= \text{weight of calcium oxide} \times 0.7147\end{aligned}$$

29.4 MAGNESIUM

There are volumetric methods available for this ion but we have not developed the necessary background. However an introduction has been given in Chapter 6 for volumetric estimation of the ion against a standard solution of EDTA (ethylenediamine tetraaceticacid) using an azo dye, Eriochrome Black T, as the end point indicator. In this section we describe a commonly used gravimetric procedure. 8-Hydroxyquinoline is a bidentate (NO) ligand which precipitates magnesium quantitatively as yellow coloured bis (8-hydroxyquinolinato) magnesium (II) from a slightly ammoniacal medium.

The given solution is treated with 2-3 gram NH_4Cl and a few drops of methyl red or methyl orange. The solution is neutralised with dropwise addition of 1 : 1 NH_4OH and thereafter made ammoniacal by the addition of a few more drops of the ammonia. The solution is heated to around 70°C and then stirred while adding drop by drop a 1% solution of 8-hydroxyquinoline in 2*N* acetic acid. As the precipitate settles and the supernatant liquid assumes a yellow colour addition of the reagent is stopped. The solution is kept warm for sometime and then filtered through a weighed sintered crucible of appropriate porosity (No. 3 or 4). The crucible is dried in an oven maintained at 100-110°C, cooled in a desiccator and weighed again. The precipitate so dried has the formula $Mg(C_9H_6ON)_2.2H_2O$ and the gravimetric factor of magnesium in this precipitate is 0.06975.

$$\text{Amount of magnesium} = \text{weight of } Mg(C_9H_6ON)_2.2H_2O \times 0.06975$$

29.5. NICKEL

Nickel is widely estimated gravimetrically as bis (dimethyl glyoximato) nickel (II) (Fig. 6.; Chapter 6). The given solution is treated with NH_4Cl and an excess of 1% solution of dimethylglyoxime in alcohol. It is then treated with dilute ammonia with stirring till the beautiful rose-red precipitate of the above nickel complex coagulates. The precipitate is digested on a steam bath for about an hour to get rid of any excess ammonia. The precipitate is then filtered through a previously weighed No. 3 or 4 sintered crucible, washed with water and dried at 120°C in an oven. The crucible is next cooled in a desiccator for about an hour and weighed. The gravimetric factor of nickel in $[Ni(C_4H_7O_2N_2)_2]$ is 0.2032.

$$\text{Amount of nickel} = \text{weight of } [Ni(C_4H_7O_2N_2)_2] \times 0.2032$$

29.6. ALUMINIUM

This ion is also estimated as tris (8-hydroxyquinolinato) aluminium (III). Since the valence of aluminium is three and the coordination number is six the precipitate has the formula stated above. Note the ligand is monobasic bidentate (NO) donor. The given solution is first treated with NH_4Cl and then made slightly ammoniacal. The reagent solution is now added dropwise with stirring till the supernatant solution assumes a yellow colour due to the reagent. The precipitate is digested for sometime and then filtered through a No. 4 sintered crucible and washed with hot water. The oxinate is then dried in an oven at 130-140°C, cooled in a desiccator and finally weighed as $[Al(C_9H_6ON)_3]$. The gravimetric factor of aluminium in the complex is 0.0587.

$$\text{Amount of aluminium} = \text{weight of } [Al(C_9H_6ON)_3] \times 0.0587$$

29.7. SILVER AND CHLORIDE

These two ions can be estimated by volumetric as well as gravimetric procedures and these methods are complementary to each other.

29.7.1. Gravimetric procedure for silver : A precipitate of AgCl appears on the addition of HCl to a solution of silver nitrate in the presence of dilute nitric acid:

$$AgNO_3 + HCl \rightarrow AgCl\downarrow + HNO_3$$

The given solution of the silver salt is treated with about 2 ml. of HNO_3. The solution is then diluted with about 200 ml. of water and then treated under stirring with a solution of 10-12 ml. of dilute ($\sim 1N$) HCl. The AgCl appears first in the colloidal form, which on warming and stirring coagulates and settles down. The precipitate is light sensitive and hence exposure to light should be minimised as far as practicable. The precipitate is allowed to stand overnight in the dark. Next morning it is filtered through a weighed sintered No. 4 crucible and the precipitate transferred and washed with $0.1N$ HNO_3 solution. After wasing several times with dilute nitric acid the crucible is dried at 120°C. After cooling in a desiccator it is weighed. The difference between the initial and final weights of the crucible gives the weight of the AgCl. The gravimetric factor of silver in AgCl is 0.7526.

$$\text{Amount of silver} = \text{weight of AgCl} \times 0.7526$$

29.7.2. Gravimetric procedure for chloride : The given chloride solution or a suitable aliquot is treated with HNO_3, diluted with water and treated under stirring with an approximately $0.1\ N$ $AgNO_3$ solution. The solution is warmed and allowed to stand overnight. The AgCl precipitate is collected and treated as above. The gravimetric factor of chloride in AgCl is 0.24737,

$$\text{Amount of chloride} = \text{weight of AgCl} \times 0.24737$$

29.7.3. Volhard's volumetric method for silver : In this procedure the silver solution is titrated by a standard solution of potassium/ammonium thiocyanate in dilute HNO_3 medium using ferric alum as indicator. As thiocyanate reacts with silver nitrate, precipitate of silver thiocyanate is formed. After all the silver ion is precipitated out excess thiocyanate reacts with ferric alum to form ferric thiocyanate. A light orange brown colour marks the end point of the titration. The reaction between silver nitrate and the thiocyanate is as shown below:

$$AgNO_3 + KSCN \rightarrow AgSCN\downarrow + KNO_3$$

The problem with this volumetric method is that the thiocyanate used is not a primary standard. Both the potassium and the ammonium salts take up water very readily and hence these cannot be used as primary standards. On the other hand silver nitrate can be obtained quite pure and can be used as a primary standard with confidence. The above reaction tells us that the equivalent weight of silver nitrate is its molecular weight. A standard ($N/10$) solution of $AgNO_3$ is made by direct weighing. An approximately ($N/10$) solution of the potassium or the ammonium thiocyanate is prepared. Ferric alum indicator is produced by adding a few drops of HNO_3 to a 40% solution of the alum.

A known volume of the standard silver nitrate solution (say 25 ml.) is taken in a conical flask. To this 4-5 ml. of $6N$ HNO_3 are added alongwith 0.5-1.0 ml. of the ferric alum indicator. Now the thiocyanate solution is added slowly from the burette while the flask is swirled. At the beginning white precipitate of AgSCN appears. Towards the end the precipitate coagulates. A permanent orange brown colour throughout the solution marks the end point of the titration.

$$\text{Strength of } AgNO_3 \times \text{volume of } AgNO_3 = \text{Strength of thiocyanate} \times \text{volume of thiocyanate}$$

$$S_1 \times V_1 = S_2 \times V_2$$

Thus the strength of the thiocyanate solution can be evaluated.

With the help of the now standardised thiocyanate solution we can easily proceed to determine the amount of silver volumetrically following the same very procedure.

$1000 \text{ ml } (N) \text{ KSCN} \equiv 1000 \text{ ml } (N)\ AgNO_3 \equiv 107.8 \text{ gram silver}$
$1 \text{ ml } (N/10)$,, $\equiv 0.010788 \text{ gram silver}$

29.7.4. Volhard's volumetric method for chloride: A standard silver nitrate solution ($N/10$) is prepared and with its help a solution of potassium thiocyanate is standardised using ferric alum as an indicator.

A known excess of the standard silver nitrate is now added to the chloride solution in presence of a few drops of HNO_3. The precipitated AgCl is allowed to coagulate and then filtered. The preciptate is washed with very dilute HNO_3 solution and the total filtrate collected. This filtrate is now titrated with the standardised KSCN solution using ferric alum as indicator. The thiocyanate solution will correspond to a certain volume, say y ml, of the standard silver nitrate solution. If the volume of the $AgNO_3$ solution taken originally is x ml then $(x-y)$ ml. is required to precipitate the chloride ion present in the solution. The chloride ion concentration can be calculated from the following relations:

$$1 \text{ ml } (N/10)\ AgNO_3 \equiv 0.00355 \text{ gram chlorine}$$

$$\text{Amount of chlorine} = \text{volume of } AgNO_3 \text{ solution} \times \text{strength of } AgNO_3 \text{ in } (N/10) \times 0.00355 \text{ gram}$$

29.8. COPPER

Both volumetric and gravimetric procedures are available for the determination of copper. However most often the volumetric (iodometric) method is adopted.

29.8.1. Volumetric method: Cupric ion is easily reduced by iodide ion in presence of a little dilute acetic acid. During this reduction iodine is liberated which can be titrated by a standard solution of sodium thiosulphate using starch as the indicator:

$$2\,CuSO_4 + 4KI \rightarrow 2CuI\downarrow + 2K_2SO_4 + I_2$$

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

$$2CuSO_4 \equiv I_2 \equiv 2Na_2S_2O_3$$

Sodium thiosulphate itself is not a primary standard. It has to be standardised by titrating the iodine liberated from KI by a known volume of a standard potassium dichromate in the presence of HCl. Details of this standardisation is given below. From the reactions given above it is seen that the equivalent weight and molecular weight of thiosulphate are the same.

Standardisation of sodium thiosulphate solution : Potassium dichromate oxidises iodide ion to free iodine in HCl medium:

$$K_2Cr_2O_7 + 6KI + 14HCl \rightarrow 2CrCl_3 + 8KCl + 3I_2 + 7H_2O$$

In the presence of the chromic ion air can readily oxidise HI to iodine:

$$KI + HCl \rightarrow HI + KCl;\ 2HI + \tfrac{1}{2}O_2 \rightarrow I_2 + H_2O$$

In order to obviate this effect the conical flask in which the oxidation reaction has to be carried out is filled with CO_2. For this purpose about 100 ml water is taken in a conical flask and 2-3 gram of $NaHCO_3$ added. 6 ml of concentrated HCl is next added and the solution swirled. The CO_2 liberated drives off the air inside the flask and ensures an atmosphere of CO_2. After the effervescence stops 25 ml of a standard (N/10) $K_2Cr_2O_7$ is added followed by 2-3 gram of KI. Now the flask is swirled very slowly and then allowed to stand in the dark for about five minutes. The sides of the flask are washed with a jet of water and the iodine is titrated with the solution of sodium thiosulphate. When the original red colour changes to a yellowish green a few drops of freshly prepared starch indicator are added. Towards the end $Na_2S_2O_3$ solution is added cautiously till the violet colour of starch-iodine is replaced by a clear green of the chromic ion. The volume of the thiosulphate is noted.

$$\text{Strength of dichromate} \times \text{volume of dichromate}$$
$$= \text{strength of thiosulphate} \times \text{volume of thiosulphate}$$

Thus the strength of the thiosulphate solution is calculated.

Titration of copper: 25 ml or a suitable aliquot of the cupric solution is taken in a conical flask and treated with 1 : 1 NH_4OH solution till the solution turns neutral or very slightly ammoniacal, as evidenced by the appearance of a light blue colour. The solution is made acidic by the addition of 2-3 ml of glacial acetic acid and is then thoroughly cooled. Now 3-4 gram KI is added and the flask swirled slowly and titration with the standard thiosulphate solution is started. As the deep yellow colour fades starch indicator and 10 ml of 2% NH_4SCN are added and the titration finished to a colourless end point. The CuI precipitate holds back some iodine. Addition of thiocyanate helps release this bound iodine and makes the titration dependable.

Amount of copper can be calculated as shown below:

$$\begin{aligned} 1000 \text{ ml of } N\ Na_2S_2O_3 &\equiv 1 \text{ gram atom of iodine} \\ &\equiv 1 \text{ gram atom of copper} \\ &\equiv 63.54 \text{ gram} \\ 1 \text{ ml } (N/10)\ Na_2S_2O_3 &\equiv 0.006354 \text{ gram copper} \end{aligned}$$

29.8.2. Gravimetric method: The cupric solution is made acidic with a few drops of dilute HCl, treated with 25-30 ml of sulphur dioxide water and 150 ml of water. The solution is now boiled and then treated with freshly prepared 10% NH_4SCN with stirring till the blue colour is completely discharged and precipitation of white cuprous thiocyanate, CuSCN, is complete. After standing for 2-3 hours the precipitate is filtered through a weighed sintered crucible No. 4. The precipitate is washed several times with a solution containing thiocyanate and sulphur dioxide (1 ml 10% NH_4SCN + some drops of SO_2 water + 100 ml water). Finally it is washed with 20-25% alcohol-water to remove excess NH_4SCN. The precipitate is then dried at 110°C, cooled in a desiccator and finally weighed. The difference between the initial and final weights gives the amount of CuSCN. The gravimetric factor of copper in CuSCN is 0.523.

$$\text{Amount of copper} = \text{weight of CuSCN} \times 0.523$$

29.9. MANGANESE

This metal is usually determined by a volumetric procedure. Manganese (II) is commonly oxidised in HNO_3 or H_2SO_4 medium by sodium bismuthate, $NaBiO_3$, to the permanganate stage:

$$2Mn^{2+} + 5NaBiO_3 + 14H^+ \rightleftharpoons 2MnO_4^- + 5Bi^{3+} + 5Na^+ + 7H_2O$$

This permanganate is next treated with a known excess of a standard ferrous ammonium sulphate and the excess ferrous is back titrated with a standard $KMnO_4$. Usually the standard solutions are of (*N*/20) strength. However if the given manganese solution contains quite a small amount then the standard solutions used are of the order of (*N*/50).

Actual procedure: The manganese solution is made 2N in HNO_3 or H_2SO_4. This is boiled with 2-3 gram $NaBiO_3$ when the manganese (II) is oxidised to purple permanganate. The solution is cooled well and treated further with another 1-2 gram of the bismuthate and stirred. The mixture is now filtered through a No. 4 sintered funnel and the residue washed with 50 ml of 2*N* H_2SO_4. $NaBiO_3$ is entirely insoluble and hence can be removed via filtration. Now a known excess of a standard (*N*/20) ferrous ammonium sulphate (usually 50 ml depending on the amount of the manganese) is run into the permanganate solution. The purple colour is immediately discharged. If the colour is not discharged another known amount of the ferrous solution has to be added. The excess ferrous is now back titrated with another standard ($N/20$) $KMnO_4$ solution and the volume noted (say y ml). Let us assume that the permanganate equivalent of the known excess of ferrous added is x ml. Then the manganese present in the given sample is equivalent to (x-y) ml of the standard $KMnO_4$ solution. The amount of manganese present in the given sample can be calculated from the following clue:

$$1 \text{ ml } (N/20)\ KMnO_4 \equiv 0.00055 \text{ gram manganese}$$

Note that because of a five electron process 1000 ml of N $KMnO_4$ is equivalent to one-fifth of one gram-atom of manganese i.e. $1/5 \times 55 = 11$ gram.

29.10. CHROMIUM

Inside the laboratory we usually need to determine chromium given in the trivalent state. In nature too chromium occurs in the same state as chromite ore: $FeO.Cr_2O_3$. Trivalent chromium is oxidised by Na_2O_2 to the hexavalent chromate:

$$Cr_2O_3 + 3Na_2O_2 = 2Na_2CrO_4 + Na_2O$$

The solution obtained by treatment with sodium peroxide is carefully heated to decompose the excess Na_2O_2 i.e. the entire oxygen has to be boiled off. The chromate solution is now cooled and then acidified with HCl to take the chromate to the dichromate form:

$$2Na_2CrO_4 + 2HCl \rightarrow Na_2Cr_2O_7 + H_2O + 2KCl$$

The dichromate solution is cooled and treated with $NaHCO_3$ so as to have a CO_2 atmosphere inside the flask. Now 2-3 gram KI is added and after little swirling the solution is allowed to stand in the dark. The liberated iodine is titrated with a standard sodium thiosulphate solution using freshly prepared starch as an indicator. The end point is marked by a change from violet to light green of chromium (III).

In this titration the oxidation number of chromium drops from + 6 to + 3. Therefore in terms of equivalents we can write that 1000 ml of N $Na_2S_2O_3$ will be equivalent to one-third of one gram-atom of chromium i.e. $1/3 \times 51.99 = 17.34$ gram.

$$1 \text{ ml } (N/10)\ Na_2S_2O_3 \equiv 0.001734 \text{ gram chromium}$$

29.11. LEAD

Lead is determined mostly by following a gravimetric procedure. $PbSO_4$ is very sparingly soluble in dilute H_2SO_4 but is substantially soluble in presence of HCl or HNO_3. Therefore the given lead solution is treated with H_2SO_4 and the solution heated on an asbestos board to dense white fumes. The dense white fumes are due to liberation of SO_3 and these ensure that all HCl or HNO_3, that might be present, are gone. The solution is maintained in this state for about 10 minutes and it is then cooled down to room temperature. 30-40 ml water is now added, stirred well and allowed to stand for an hour. The $PbSO_4$ is filtered through a No. 4 sintered funnel, washed several times with 1% H_2SO_4 and finally with rectified spirit. The sintered funnel is dried at 125-130°C and weighed. The gravimetric factor of lead in lead sulphate is 0.6833.

$$\text{Amount of lead} = \text{weight of } PbSO_4 \times 0.6833$$

29.12. ZINC

Zinc (II) may be precipitated as zinc ammonium phosphate, $Zn(NH_4)PO_4$. It may be dried at ~100°C and weighed in this form or ignited to the pyrophosphate $Zn_2P_2O_7$ and weighed in that form.

Actual procedure: A suitable aliquot (say 50 ml) of the zinc (II) solution is taken in a beaker. 1 ml concentrated HCl and a few drops of methyl red indicator are added. The solution is neutralised with dropwise addition of 1 : 1 NH_4OH. 100 ml of water is added and the solution brought to boil. 25 ml of 10% diammonium hydrogen phosphate is added slowly with stirring when zinc ammonium phosphate is precipitated. The precipitate is kept warm for an hour, then cooled and filtered through No. 4 sintered funnel. The precipitate is washed with a solution of 1 % diammonium hydrogen phosphate and finally with 1 : 1 alcohol-water. The precipitate is dried at 100-105°C, cooled in a desiccator and weighed. The gravimetric factor of zinc in $Zn(NH_4)PO_4$ is 0.3665.

$$\text{Amount of zinc} = \text{amount of } Zn\,(NH_4)PO_4 \times 0.3665$$

If the estimation is to be done as pyrophosphate then the precipitate of $Zn(NH_4)PO_4$ is filtered through No. 42 filter paper, washed as described above and ignited in weighed silica crucible to $Zn_2P_2O_7$. The gravimetric factor of zinc in the pyrophosphate is 0.4291.

$$\text{Amount of zinc} = \text{weight of } Zn_2P_2O_7 \times 0.4291$$

EXERCISES

1. Explain the utility of stannous chloride, mercuric chloride, and phosphoric acid in the volumetric estimation of iron. Do we need to use Zimmermann-Reinhardt solution if we use potassium dichromate in the determination of iron?
2. Present a comparative assessment of potassium dichromate and potassium permanganate in the determination of iron.
3. What is the difference between volumetric analysis and gravimetric analysis? What is the meaning of gravimetric factor?
4. You are given a mixture of iron and copper. How would you proceed to determine the constituents?
5. A solution contains both ferrous and ferric iron. How would you determine the two constituents?
6. You are given a mixture of lead and copper. Suggest a procedure for the estimation of the two metals gravimetrically.
7. How are potassium permanganate and sodium thiosulphate standardised? What are their equivalent weights?
8. Suggest a procedure for the determination of iron and calcium present in a mixture.
9. Give a brief account of the gravimetric estimations of iron, copper, magnesium and zinc.
10. How would you proceed to estimate the following metals present in the binary mixtures (*a*) iron and nickel and (*b*) nickel and chromium?

CHAPTER 30

SOME CHEMICAL PROBLEMS

30.1. PROBLEMS RELATED TO ATOMIC WEIGHT

Problem 1: 1.26 gram of a metal oxide MO is reduced with hydrogen and 1.019 gram of the metal is obtained. Calculate the equivalent weight and the atomic weight of the metal.

The weight of oxygen in the oxide $= 1.26 - 1.0019 = 0.241$ gram

The equivalent weight of the metal will be that weight which will correspond to 8 gram of oxygen. Therefore the equivalent weight is:

$$\text{Equivalent weight} = \frac{1.019 \times 8}{0.241} = 33.8 \text{ gram.}$$

Since the formula of the oxide is MO the metal is bivalent. Hence the atomic weight is double the equivalent weight.

$$\text{Atomic weight} = 2 \times 33.8 = 67.6$$

Problem 2: Specific heat of a metal is 0.079 Cal/g°C. The gram equivalent weight of the metal is 23.24. Find out the gram atomic weight of the metal.

According to Dulong and Petit law the product of specific heat and gram atomic weight is roughly 6 Cal/g°C. Again gram atomic weight is given by the product of the valence (n) and gram equivalent weight.

Therefore $n \times 23.24 \times 0.079$ Cal/g°C $= 6$ Cal/g°C
Hence $n \simeq 3$; gram atomic weight $= 3 \times 23.24 = 69.72$ gram

Problem 3: Specific heat of a metal is 0.086 Cal/g°C. Gram equivalent weight of the metal is 23.24 gram. Calculate its atomic weight. (Answer: 69.72 gram)

Problem 4: 12.0 gram of a metal is heated to 50°C and then dropped into 10.0 gram of water. The temperature of water goes up from 25°C to 27.8°C. The oxide of this metal contains 30.1% oxygen. Calculate the gram atomic weight, gram equivalent weight and valence of the metal.

I. Gram atomic weight: The specific heat of water $= 1$ Cal/g°C. The amount of heat absorbed by the 10.0 gram water

$$= 1.00 \text{ Cal/g°C} \times 10.0\text{g} \times (27.8 - 25.0)\text{°C} = 28 \text{ Cal}$$

Therefore 28 Cal = specific heat of the metal × 12.0 g × (50—27.8)°C.
Specific heat = 0.11 Cal/g°C.

$$\text{Gram atomic weight} = \frac{6 \text{ cal/g°C}}{0.11 \text{cal/g°C}} = 55 \text{ gram}$$

Recall that the product of the specific heat and gram atomic weight is approximately 6 Cal/g°C.

II. Gram equivalent weight: Percentage of the metal in its oxide is

$$= (100-30.1) = 69.9 \text{ gram}.$$

Gram equivalent weight will be that weight which will correspond to 8 gram of oxygen. Hence:

$$\text{Gram equivalent weight} = \frac{8.00 \times 69.9}{30.1} = 18.6 \text{ gram}$$

III. Valence is gram atomic weight divided by gram equivalent weight and it should be the nearest whole number.

$$\text{Valence} = 55/18.6 \simeq 3 = 3$$

Problem 5: A metal chloride contains 54.7% chlorine by weight. If the metal and chlorine ratio is 1 : 1 then what is the atomic weight of the metal? If the ratio is 1 : 2 then what will be the atomic weight of the metal?

(Answer: 29.4 for 1 : 1; 58.8 for 1 : 2)

Problem 6: Gram molecular weight of oxygen is 32. What is the weight of one atom of oxygen?

One gram molecular weight of any substance contains one Avogadro number i.e. 6.02×10^{23} molecules. Therefore one molecule of oxygen weighs $(32 \text{ gram}/6.02 \times 10^{23}) = 5.3 \times 10^{-23}$ gram. Sine oxygen is diatomic hence the weight of one oxygen atom will be half this weight i.e. 2.65×10^{-23} gram.

Problem 7: One gram mole of methane weighs 16 gram. Calculate the weight of one molecule of methane. (Answer: 2.66×10^{-23} gram)

Problem 8: 1.7301 gram of a trivalent metal reacts with excess oxygen to give 2.2015 gram of the oxide. Calculate the atomic weight of the metal.

The reaction is: $2M + 3O \rightarrow M_2O_3$

Let the atomic weight be x. Then $2x$ gram of the metal react with $3 \times 16 = 48$ gram of oxygen.

Therefore the following relation will hold:

$$\frac{2x+48}{2x} = \frac{2.2015}{1.7301}$$

$$2x \times 2.2015 = 1.7301 \times (2x + 48)$$

$$4.4030x = 3.4602x + 83.0448; \quad \therefore x = 88.0$$

Alternatively we can find out the equivalent weight of the metal and multiply by 3 to get the atomic weight.

Since 1.7301 gram of the metal reacts with $(2.2015-1.7301) = 0.4714$ gram of oxygen we have:

$$\text{Equivalent weight} = \frac{1.7301 \times 8}{0.4714} = 29.35$$

$$\text{Atomic weight of the metal} = 29.35 \times 3 = 88 \text{ gram}$$

Problem 9: 0.408 gram of a pentavalent metal reacts with oxygen to give 0.728 gram oxide. Calculate the atomic weight of the metal. Name the metal from the Table of atomic weights given in Appendix. (Answer: 51; vanadium)

Problem 10: An evacuated bulb is filled with oxygen at 16°C and 740 mm pressure. The difference between the weights of the evacuated bulb and the oxygen filled bulb is 0.4663 gram. The volume of the bulb is 355 ml. Calculate the molecular weight of oxygen.

Standard temperature and pressure are 273°K and 760 mm.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Volume of the oxygen under standard temperature and pressure

$$= \frac{740 \times 355 \times 273}{760 \times 289} \text{ ml.}$$

From Avogadro hypothesis we know that at standard temperature and pressure one gram mole of oxygen will occupy 22.4 litres. The weight of one gram mole i.e. of 22.4 litres will be given by:

$$\frac{0.4663 \times 22400 \times 760 \times 289}{355 \times 740 \times 273} = 32.0 \text{ gram}$$

Hence the molecular weight of oxygen works out to be 32.0.

30.2. PROBLEMS RELATED TO EQUIVALENT WEIGHT

Problem 1: 0.1827 gram of the chloride of an element corresponds to 0.1057 gram of the oxide. Calculate the equivalent weight of the element.

We have to appreciate that chloride ion is monovalent while oxide ion is bivalent. This means one atom of chlorine is equivalent to $\frac{1}{2}$ atom of oxygen. If the element has x as its equivalent weight then the following ratios will hold:

$$\frac{x + 35.5}{x + 8} = \frac{0.1827}{0.1057} = 1.73 \text{ (equivalent weights of chlorine and oxygen are 35.5 and 8)}$$

$$x + 35.5 = 1.73\,(x + 8)\ ;\quad x = 29.6$$

Problem 2: 2.00 gram of nickel oxide is reduced by hydrogen and 1.572 gram of the metal is thereby produced. Find out the equivalent weight of nickel.

Amount of oxygen in nickel oxide = 2.00−1.572 = 0.428 gram. The weight corresponding to 8 gram of oxygen will be the equivalent weight of nickel.

$$\text{Equivalent weight} = \frac{1.572 \times 8}{0.428} = 29.4 \text{ gram.}$$

Problem 3: 1.083 gram of mercuric oxide gives on heating 1.003 gram of mercury. Calculate the equivalent weight of mercury.

The weight of oxygen in mercuric oxide = 1.083—1.003 = 0.08 gram

$$\text{The equivalent weight} = \frac{1.003 \times 8}{0.08} = 100 \text{ gram}$$

Problem 4: 2.00 gram calcium oxide on treatment with HCl gives 3.962 gram calcium chloride. Find the equivalent weight of calcium.

The equivalent weights of chlorine and oxygen are 35.5 and 8 respectively. Taking x as the equivalent weight of calcium the following relation can be put down:

$$\frac{x+35.5}{x+8} = \frac{3.962}{2.00} = 1.981$$

$$x + 35.5 = 1.981\,(x + 8)\ ;\quad x = 20.05$$

Thus the equivalent weight of calcium works out to be 20.05.

Problem 5 : On treating 2.6 gram zinc metal with dilute H_2SO_4 888.8 ml of hydrogen is evolved under standard temperature and pressure. Calculate the equivalent weight of the metal.

One gram molecule of hydrogen will occupy 22.4 litres at standard temperature and pressure. But hydrogen is diatomic. One equivalent of zinc will correspond to one gram atom of hydrogen or to $\frac{1}{2}$ gram mole of hydrogen. So that weight of zinc which will liberate $\frac{1}{2} \times 22400$ ml of hydrogen will be its equivalent weight.

$$\text{Equivalent weight of zinc} = \frac{2.6 \times \frac{1}{2} \times 22400}{888.8} = 32.76$$

Problem 6 : 0.176 gram of a bivalent metal gives with HCl 190 ml of hydrogen at 27°C and 720 mm pressure. Calculate the equivalent weight and atomic weight of the metal.

Since the metal is bivalent one gram atom will give two gram atoms i.e. one gram molecule of hydrogen i.e. 22.4 litres at standard temperature and pressure.

$$\text{Volume of hydrogen at S.T.P.} = \frac{720 \times 190 \times 273}{300 \times 760}$$

$$\text{Gram atomic weight of the metal} = \frac{0.176 \times 300 \times 760 \times 22400}{720 \times 190 \times 273} = 24$$

$$\text{Equivalent weight} = \text{atomic weight/valence} = 24/2 = 12$$

30.3. PROBLEMS RELATED TO CHEMICAL FORMULA

Problem 1: Percentage of sulphur in a binary compound of sulphur and nitrogen is 69.59%. Find the empirical composition of the compound.

$$\%\ \text{sulphur} = 69.59;\ \%\ \text{nitrogen} = 100-69.59 = 30.41$$

If we divide these figures by the respective atomic weights we will get the number of gram atoms of the elements present per 100 gram of the compound.

$$\text{gram atom of sulphur} = 69.59/32.06 = 2.17$$

$$\text{gram atom of nitrogen} = 30.41/14.01 = 2.17$$

Thus the same gram atoms of the two elements are present in the compound. Thus the emipirical composition of the compound is SN.

Problem 2: The percentages of nitrogen and oxygen in a binary compound are 25.94 and 74.06. Find the composition.

Dividing by the respective atomic weights we arrive at the gram atoms of the two elements per 100 gram of the sample.

gram atom of nitrogen = 25.94/14.01 = 1.85
gram atom of oxygen = 74.06/16.00 = 4.63

Thus the empirical composition is $N_{1\cdot85}\,O_{4\cdot63}$. Since we must have only whole numbers of atoms reacting we divide the figures by 1.85 in order to make the atom number of nitrogen as 1. Thus the formula of the compound is:

$$N_{1\cdot85/1\cdot85}\,O_{4\cdot63/1\cdot85} \text{ i.e. } N_1O_{2\cdot5}.$$

By doubling the numbers we get whole numbers of atoms for both the elements. Thus the true composition is N_2O_5.

Problem 3: A compound made of sodium, sulphur and oxygen has the percentages of sodium and sulphur as 32.4 and 22.5. Find the composition.

gram atom of sodium = 32.4/23 = 1.4
gram atom of sulphur = 22.5/32 = 0.7
gram atom of oxygen = [100−(32.4 + 22.5)]/16 = 2.82

The empirical composition is $Na_{1\cdot4}\,S_{0\cdot7}O_{2\cdot82}$ i. e. Na_2SO_4.

Problem 4: A compound contains 43.4% sodium, 11.3% carbon and the rest is oxygen. Find the composition. (Answer: Na_2CO_3)

Problem 5: A hydrocarbon compound contains 80.0% carbon and 20% hydrogen. If the molecular weight is close to 30 what is the formula? (Answer: CH_3; C_2H_6)

Problem 6: A binary compound contains 79.8% chlorine and the rest aluminium. If the molecular weight is close to 270 what is the formula? (Answer: Al_2Cl_6)

Problem 7: A compound containing potassium, oxygen and sulphur has 44.82% potassium and 36.78% oxygen. Find its composition. (Answer: K_2SO_4)

Problem 8: A sample of limestone contains 70% $CaCO_3$. How much quicklime can be had from 16 tons of such limestone if the thermal decomposition efficiency is 92%?

$$\underset{(100)}{CaCO_3} \rightarrow \underset{(56)}{CaO} + CO_2$$

If the sample is 100% pure then 100 ton would give 56 ton CaO. Therefore 16 tons of the given sample contains (70 × 16)/100 = 11.2 tons $CaCO_3$.

If the thermal decomposition were 100% efficient we would get:

$$CaO = (56 \times 11.2)/100 = 6.2 \text{ tons}$$

Since the efficiency is 92% the actual amount of CaO = (92 × 6.2)/100 = 5.70 ton.

Problem 9: A compound composed of sulphur, chlorine and oxygen has 23.76% sulphur, and 52.54% chlorine. The vapour density of the compound is 68. Find the composition.

We first work out the gram atoms present per 100 gram of the compound:

gram atom of sulphur $= 23.76/32 = 0.74$
gram atom of chlorine $= 52.54/35.5 = 1.50$
gram atom of oxygen $= 23.70/16 = 1.48$

The empirical composition is $S_{0.74}\,Cl_{1.50}\,O_{1.48}$ i.e. SO_2Cl_2. Since the vapour density is 68 the molecular weight has to be double i.e. 136. The molecular weight as calculated from the formula SO_2Cl_2 is 135. Thus the true formula is SO_2Cl_2 i.e. the compound is sulphonyl chloride.

30.4. PROBLEMS RELATED TO ELECTROLYSIS

In Chapter 7 we have worked out several problems on Faraday's laws of electrolysis. Here we work out only three problems and give merely the answers of four more.

Problem 1: On electrolysis of nickel sulphate solution nickel is deposited at the cathode while oxygen is evolved at the anode. Calculate (a) the gram equivalents of nickel and oxygen and (b) gram of nickel and oxygen on the passage of 38,200 coulombs of electricity (atomic weight of Ni, 58.7).

Nickel sulphate is $NiSO_4(7H_2O)$. Both nickel (II) and oxide ion are bivalent. The reactions at the cathode and at the anode are:

at the cathode: $Ni^{2+} + 2e \rightarrow Ni$

at the anode: $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e$

We know from Faraday's laws that passage of one *faraday* i.e. 96,500 coulombs of electricity can lead to the deposition or discharge of one gram equivalent. Since the ions concerned are bipositive and binegative their equivalent weights are half the atomic weights.

$$\text{(a) gram equivalent of nickel deposited} = \frac{38{,}200 \text{ coulombs}}{96{,}500 \text{ coulombs}} = 0.396$$

$$\text{gram equivalent of oxygen} = \frac{38{,}200 \text{ coulombs}}{96{,}500 \text{ coulombs}} = 0.396$$

$$\begin{aligned}\text{(b) weight of nickel deposited} &= 0.396 \times \text{equivalent weight}\\ &= 0.396 \times (58.72/2) = 11.6 \text{ gram}\end{aligned}$$

$$\begin{aligned}\text{weight of oxygen} &= 0.396 \times \text{equivalent weight}\\ &= 0.396 \times (16/2) = 3.17 \text{ gram}\end{aligned}$$

Problem 2: How much cobalt is deposited at the cathode on the passage of 0.6 ampere current for one hour through a cobalt chloride solution? What should be the ampere if we wish to deposit one gram cobalt per minute? (atomic weight of cobalt, 58.9).

at the cathode: $Co^{2+} + 2e \rightarrow Co$

gram equivalent weight $= 58.9/2 = 29.45$ gram

For the deposition of 29.45 gram of cobalt we need one *faraday* of electricity i.e. 96,500 coulombs.

0,6 ampere for 1 hour $= 0{,}6 \times 60 \times 60$ coulombs

Amount of cobalt deposited = (29.45 gram × 0.6 × 60 × 60 coulombs)/ 96,500 coulombs = 0.660 gram.

For a deposition of 29.45 gram cobalt we need 96,500 coulombs
,, ,, 1.00 ,, ,, (96,500 colombs/29.45)

Let us assume the required ampere is x. Then we can write:

$$\frac{96{,}500 \text{ coulombs}}{29.45} = x \text{ ampere} \times 1 \text{ minute} = x \times 60 \text{ coulombs}$$

$$\text{Thus } x = \frac{96{,}500}{29.45 \times 60} = 54.7 \text{ ampere}$$

Problem 3: On the passage of the same quantity of electricity 12.9 gram of copper and 16.8 gram of another metal are obtained. Find out the gram equivalent weight of the metal (atomic weight of copper, 63.5).

Since the same quantity of electricity has been passed therefore according to Faraday's second law the weights of the two metals will bear the same ratio as their gram equivalent weights. But we have to bear it in mind that cupric ion is bipositive and hence its equivalent weight is half its atomic weight. Thus we can write:

$$\frac{12.9}{16.8} = \frac{\frac{1}{2} \times 63.5}{x} \quad (x = \text{gram equivalent weight of the other metal})$$

$$x = \frac{16.8 \times 63.5 \times \frac{1}{2}}{12.9} = 41.4 \text{ gram}$$

Problem 4: 12.02 gram of a brass containing 62.3% copper is dissolved in HNO_3 and the solution electrolysed. With a current of 0.542 ampere how long will it take to deposit the entire amount of the copper at the cathode?

(Answer: 11.7 hours)

Problem 5: A solution of Al_2O_3 in fused cryolite is electrolysed with a current of 25 ampere. How much aluminium will be deposited per hour?

(Answer: 8.38 gram)

Problem 6: A salt of lanthanum (atomic weight 138.9) is electrolysed. After electrolysis for an hour with 1.93 ampere 3.33 gram of the metal is obtained at the cathode. What is the valence of the lanthanum ion? (Answer: trivalent)

Problem 7: Chloride salt of gadolinium (atomic weight 157) is electrolysed. After the passage of 3216 coulombs 1.74 gram is deposited at the cathode. Determine the charge on the ion. (Answer: + 3)

30.5. PROBLEMS RELATED TO GASES

Problem 1: 0.0625 gram of nitrogen occupies 50 ml under standard temperature and pressure. Determine the molecular weight of the gas.

One gram mole of any gas occupies at standard temperature and pressure 22.4 litres. Thus the molecular weight of nitrogen is given by (0.0625 × 22400)/ 50 = 28 gram.

Problem 2: During some chemical reaction 0.2560 gram of oxygen is liberated. The gas is collected over water. The volume of the gas is 207 ml. Temperature and aqueous tension are 27°C and 26.7 mm. If the barometric pressure is 749 mm find the molecular weight of oxygen.

We have to work out the volume of the liberated oxygen under standard temperature and pressure.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\text{; therefore } \frac{(749-26.7) \times 207}{273+27} = \frac{760 \times V_2}{273}$$

$$V_{\text{S.T.P.}} = V_2 = \frac{273 \times (749-26.7) \times 207}{760 \times (273+27)} = 179 \text{ ml}$$

$$\text{Therefore molecular weight of oxygen} = \frac{0.2560 \times 22400}{179} = 32.0$$

Problem 3: A mixture of $CaCO_3$ and $MgCO_3$ gives 240 ml of CO_2 per gram of the mixture under standard temperature and pressure. Determine the ratio of the two carbonates (molecular weights: $CaCO_3$, 100; $MgCO_3$, 84).

Let us assume that the amount of $CaCO_3$ in the mixture is x gram. Then the amount of $MgCO_3$ is $(1-x)$ gram. Now consider the reactions.

$$\underset{(100\text{ gram})}{CaCO_3} \rightarrow CaO + \underset{(22.4\text{ litres})}{CO_2}$$

$$\underset{(84\text{ gram})}{MgCO_3} \rightarrow MgO + \underset{(22.4\text{ litres})}{CO_2}$$

x gram $CaCO_3$ will give $(x \times 22400)/100 = 224x$ ml.

$(1-x)$ gram $MgCO_3$ will give $(1-x) \times 22400/84 = (266-266x)$ ml

Therefore $224x + 266 - 266x = 240;\ x = 0.62$

Thus $CaCO_3 = 0.62$ gram; $MgCO_3 = 1-0.62 = 0.38$ gram

Therefore $MgCO_3 : CaCO_3 = 0.38 : 0.62 = 3;\ 5$

Problem 4: 500 ml of a mixture of CO and CO_2 is reduced by carbon to 800 ml of CO. Assuming the temperature and pressure remain the same before and after the experiment determine the amount of CO and CO_2 in the original mixture.

$$CO_2 + C \rightarrow 2CO$$

At standard temperature and pressure both CO and CO_2 will occupy 22.4 litres per gram mole. But the reaction shows that one gram mole of CO_2 produces two gram moles of CO. Let us assume that the amount of CO in the mixture is x ml. Then the volume of CO_2 is $(500-x)$ ml. This CO_2 will produce $2\,(500-x)$ ml of CO on reduction by charcoal.

Therefore $x + 2\,(500-x) = 800$ ml.; $x = 200$ ml

Thus the volume of CO in the mixture is 200 ml and the rest i.e. 300 ml is CO_2.

30.6. PROBLEMS RELATED TO ACIDS AND BASES

Problem 1: 22.3 ml of an 0.24*M* NaOH solution is required to neutralise 50.0 ml of a vinegar solution (i.e. a solution of acetic acid). Calculate the concentration of acetic acid in the vinegar sample.

We first calculate how many moles of NaOH are present in the NaOH solution.

$$\text{Moles of NaOH} = \frac{0.24 \text{ moles} \times 0.223 \text{ litre}}{1 \text{ litre}} = 0.005352 \text{ moles}$$

The neutralisation reaction is:

$$\underset{(1\text{ mole})}{CH_3COOH} + \underset{(1\text{ mole})}{NaOH} \rightarrow CH_3COONa + H_2O$$

It follows therefore that 50 ml of the vinegar contains 0.005352 moles of acetic acid.

Therefore concentration of acetic acid in the vinegar

$$= \frac{0.005352 \text{ moles} \times 1000 \text{ ml}}{50 \text{ ml}} = 0.106\ M$$

Problem 2: 24.0 ml of 0.20*M* HCl solution is needed to neutralise 0.5 gram of a mixture of $Ca(OH)_2$ and $CaCl_2$. Calculate the percentage of $Ca(OH)_2$ in the mixture (atomic weight of Ca, 40).

The neutralisation reaction is : $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$

This means the number of moles of $Ca(OH)_2$ will be half the moles of HCl required for the neutralisation.

Moles of HCl = (0.2 moles/litre) × 0.024 litre = 0.0048 moles

Moles of $Ca(OH)_2$ = $\frac{1}{2}$ × 0.0048 = 0.0024 moles

Weight of $Ca(OH)_2$ = (gram molecular weight/mole) × 0.0024 moles

= 74 × 0.0024 gram = 0.178 gram

Percentage of $Ca(OH)_2$ in the mixture = (0.178 × 100)/0.5 = 35.6%

Problem 3: 20.0 ml of 0.10 *M* NaOH is needed to neutralise 1.00 gram of a sample containing benzoic acid. Determine the percentage of benzoic acid in the sample.

Benzoic acid, C_6H_5COOH, is a monobasic acid and NaOH is a monoacidic base. So equimolar proportions will be required in their neutralisation.

Moles of NaOH = (0.1 moles/litre) × 0.02 litre = 0.002 moles

Molecular weight of benzoic acid = 122

Moles of benzoic acid present in the sample = 0.002 moles

Percentage of benzoic acid = (122 gram/mole) × 0.002 mole × (100/1 gram)

= 24.4%.

Problem 4: 22.6 ml 0.254*M* NaOH is required to neutralise 0.466 gram of an acid. Calculate the equivalent weight of the acid. (Answer: 81.6 gram)

Problem 5: 20.0 ml of 0.18*M* HCl is required to neutralise 0.324 gram of a mixture of NaCl and Na_2CO_3. Calculate the percentage of Na_2CO_3 in the mixture. (Answer: 59%)

Problem 6: 125 ml of a dilute sulphuric acid reacts with excess FeS to give 560 ml of H_2S at standard temperature and pressure. Calculate the normality of the acid.

As we know the reaction is: $FeS + H_2SO_4 \rightarrow H_2S + FeSO_4$
One gram mole i.e. two equivalents i.e. 1000 ml of $2N$ H_2SO_4 will liberate one gram mole i.e. 22400 ml of H_2S at S.T.P.

$$22400 \text{ ml of } H_2S \equiv 1000 \text{ ml of } 2N\ H_2SO_4$$

$$560 \quad ,, \quad ,, \quad \equiv \frac{1000 \times 2 \times 560}{22400} \text{ ml of } N\ H_2SO_4$$

$$\equiv 50 \text{ ml of } N\ H_2SO_4$$

Therefore 125 ml $\times\ x = 50$ ml $N\ H_2SO_4$ (x is assumed to be the normality of the sulphiric acid)

$$x = 0.4N\ H_2SO_4$$

Problem 7: 0.21 gram of a metal is dissolved in 100 ml of $0.5N$ H_2SO_4. The excess acid is neutralised by 32.5 ml of N alkali. Calculate the equivalent weight of the metal.

Equivalent weight of the metal is the weight corresponding to 1000 ml of $N\ H_2SO_4$. Our duty is to know how much of the given acid reacted with the metal.

32.5 ml N alkali $\equiv 2 \times 32.5$ of $0.5N\ H_2SO_4 \equiv 65$ ml of $0.5N\ H_2SO_4$

Therefore (100−65) = 35 ml of $0.5N$ acid reacted with the metal.

35 ml $0.5N$ acid $\equiv 17.5N$ acid

Therefore the equivalent weight of the metal $(0.21 \times 1000)/17.5 = 12$ gram

Problem 8: A mixture of $NaHCO_3$ and Na_2CO_3 weighing 0.475 gram requires 15 ml of $0.5N$ H_2SO_4 for neutralisation using methyl orange as an indicator. Calculate the percentage of Na_2CO_3. (Answer: 56.46%)

30.7 PROBLEMS RELATED TO SOLUBILITY PRODUCT AND COMMON ION EFFECT

Problem 1: Solubility of barium sulphate (molecular weight 233) at 25°C is 0.00023 gram per 100 ml of water. Calculate the solubility product.

We have to calculate the solubility of barium sulphate in terms of gram moles.

$$\text{Solubility per litre} = \frac{0.00023 \text{ gram} \times 1000}{100 \times 233} = 1 \times 10^{-5} \text{ moles/litre}$$

Each molecule of $BaSO_4$ breaks up into one Ba^{2+} and one SO_4^{2-} ion.

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

$$[Ba^{2+}] = [SO_4^{2-}] = 1 \times 10^{-5}$$

$$\text{Solubility product } K_{SP} = [Ba^{2+}][SO_4^{2-}] = 1 \times 10^{-5} \times 1 \times 10^{-5}$$

$$= 1 \times 10^{-10}$$

Problem 2: Solubility of silver chromate (molecular weight 332) is 0.0279 gram per litre at 25°C. Calculate its solubility product.

Solubility of Ag_2CrO_4 in molarity = $(0.20279/332) = 8.4 \times 10^{-5}$ moles/litre.

Ag_2CrO_4 dissociates to give two Ag^+ ions and one CrO_4^-. Molarity of Ag_2CrO_4 and CrO_4^{2-} is the same but that of the Ag^+ ion is just the double.

$$[Ag^+] = 2 \times 8.4 \times 10^{-5} = 1.7 \times 10^{-4}$$

$$[CrO_4^{2-}] = 8.4 \times 10^{-5}$$

$$\text{Solubility product } K_{SP} = [Ag^+]^2\,[CrO_4^{2-}] = (1.7 \times 10^{-4})^2 \times 8.4 \times 10^{-5} = 2.4 \times 10^{-12}$$

Problem 3: Solubility product of CaF_2 is 4×10^{-11}. Determine the solubility of CaF_2 in moles per litre in (a) water (b) $0.01M$ $CaCl_2$ and (c) $0.01M$ NaF.

(a) In saturated solution we can write the following:

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

Assuming the solubility of CaF_2 as s we can write: $[Ca^{2+}] = s$; $[F^-] = 2s$

$$K_{SP} = [Ca^{2+}]\,[F^-]^2 = s.(2s)^2 = 4s^3 = 4 \times 10^{-11}$$

Therefore the solubility in water $s = (4 \times 10^{-11}/4)^{\frac{1}{3}} = 2.15 \times 10^{-4}$ moles/litre

(b) In $0.01M$ $CaCl_2$ $[Ca^{2+}] = 0.01M$

Total calcium $= 0.01 + s$; $[F^-] = 2s$ (s = solubility of CaF_2)

Therefore $(0.01 + s)(2s)^2 = 4 \times 10^{-11}$

Since $s \ll 0.01$ we can simply write:

$$0.01 \times 4s^2 = 4 \times 10^{-11};\ s = 3.2 \times 10^{-5} \text{ moles/litre}$$

(c) $[Ca^{2+}] = s$; $[F^-] = (2s + 0.01)$

Therefore $s(2s + 0.01)^2 = 4 \times 10^{-11}$

We can easily appreciate that here too $2s \ll 0.01$

Therefore $s \times 10^{-4} = 4 \times 10^{-11}$; $s = 4 \times 10^{-7}$ moles/litre

Problem 4: The hydrogen ion concentration of a 100 ml solution of $0.10M$ Cu^{2+} and Mn^{2+} is $0.20M$. This solution is saturated with H_2S. Which of the two sulphides will be precipitated? (K_{SP} : CuS, 4×10^{-45}; MnS, 1×10^{-16}; K_1 and K_2 of H_2S are 1×10^{-7} and 1×10^{-15}; $H_2S \simeq 0.1$).

$$H_2S \rightleftharpoons H^+ + HS^-\ ;\ K_1 = \frac{[H^+]\,[HS^-]}{[H_2S]} = 1 \times 10^{-7}$$

$$HS^- \rightleftharpoons H^+ + S^{2-}\ ;\ K_2 = \frac{[H^+]\,[S^{2-}]}{[HS^-]} = 1 \times 10^{-15}$$

$$[S^{2-}] = \frac{K_2\,[HS^-]}{[H^+]} = \frac{K_2K_1\,[H_2S]}{[H^+][H^+]} = \frac{K_2K_1\,[H_2S]}{[H^+]^2}$$

Concentration of H_2S in a saturated solution is $\simeq 0.1M$. Therefore:

$$[S^{2-}] = \frac{K_1K_2 \times 0.1}{[H^+]^2} = \frac{1 \times 10^{-7} \times 1 \times 10^{-15} \times 10^{-1}}{[H^+]^2} = \frac{1 \times 10^{-23}}{[H^+]^2}$$

Hydrogen ion concentration in our given solution is $0.2M$. Therefore:

$$[S^{2-}] = \frac{1 \times 10^{-23}}{(0.20)^2} = 2.5 \times 10^{-22}$$

Concentration of copper (II) $= 0.10M$

$$[Cu^{2+}] \times [S^{2-}] = 0.10 \times (2.5 \times 10^{-22}) = 2.5 \times 10^{-23} \gg 4 \times 10^{-45}$$

$$[Mn^{2+}]\,[S^{2-}] = 0.10 \times (2.5 \times 10^{-22}) = 2.5 \times 10^{-23} \ll 1 \times 10^{-16}$$

Thus CuS will be precipitated but not MnS.

APPENDIX I

STRUCTURES OF THREE IMPORTANT TYPES OF IONIC COMPOUNDS

While discussing the nature of the chemical bond (Chapter 5) we have already observed some very fundamental differences between ionic and covalent compounds. In covalent compounds there exist discrete molecules held together by weak van der Waals' forces. But in ionic compounds no such discrete molecules exist—instead giant molecules are formed as a result of electrostatic attraction between oppositely charged ions. The internal structure of ionic compounds depend on several factors. Important ones among these are the following:

(a) interaction between different types of atoms

(b) differing sizes of the interacting atoms

(c) difference in the electronegativities of the interacting elements

Over and above these factors things become complicated because of the various stoichiometries found. In this short discussion we shall keep us confined to the simplest of stoichiometries, namely AB type compounds with 1 : 1 interaction. Even then we will see that the above three factors are sufficient enough to give rise to compounds of sufficient complexities. We take three AB type compounds: NaCl, CsCl and ZnS. Although all the three compounds are of the AB types it should be appreciated that there do exist differences in sizes, electronegativities and charges of the atoms concerned and these result in very different structures of the compounds (Fig I.1).

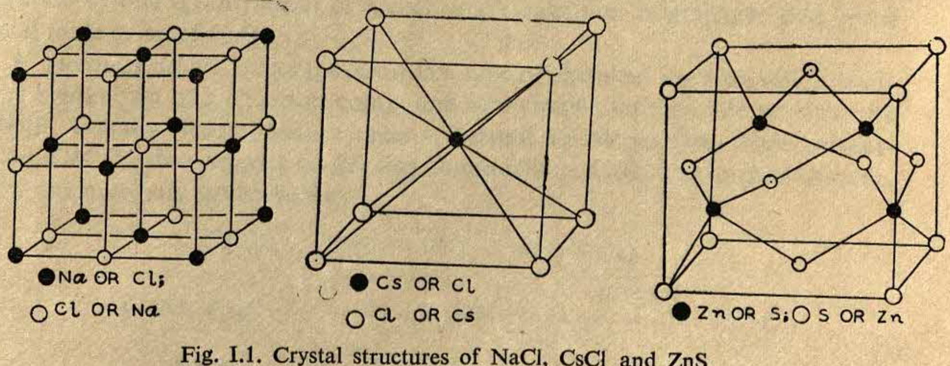


Fig. I.1. Crystal structures of NaCl, CsCl and ZnS

Since ionic compounds are made up of oppositely charged ions these tend to attract as many of the other kind as possible about them. Thus the crystallographic coordination number is very much dependent on the size of the cation and the anion i.e. on the ratio of cation radius to the anion radius.

Sodium Chloride (*NaCl*): X-ray structural investigations have conclusively shown that in sodium chloride crystal each sodium ion is surrounded by as many as six chloride ions and vice versa. The six chloride ions surround the sodium ion at the six corners of a regular octahedron at the centre of which is the sodium ion. Similarly each chloride ion is octahedrally surrounded by six sodium ions. Thus electroneutrality is established. Such 6 : 6 octahedral structures are found in LiF, LiCl., LiBr, NaF, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl. The ratio of the cation radius: anion radius is the final yardstick in deciding the nature of the ionic crystal structure. It has been calculated that *NaCl crystal structure results when the cation: anion radius ratio varies within the range* 0.414 *to* 0.732.

Caesium Chloride (*CsCl*): It is worthwhile to appreciate at the very outset that the caesium ion is very much larger than sodium ion: the cation radii are 0.95A for Na^+ and 1.69A for Cs^+. Thus it can be followed that a monopositive caesium ion can accommodate more chloride ions about it. In reality it is found that each caesium ion is surrounded by as many as eight chloride ions at the corners of a regular cube, the centre of which is occupied by the caesium ion. Similarly each chloride ion is also surrounded by eight caesium ions to maintain electroneutrality. Such structure results when the cation: anion radius ratio exceeds 0.732. This 8:8 structure is found in CsCl, CsBr, CsI, NH_4Cl, NH_4Br.

Zinc Sulphide (*Zinc Blende*)(*ZnS*) : This is an AB type compound no doubt but both the cation and the anion are bivalent. Their sizes are also very different because of the double charge. Each zinc (II) ion is surrounded tetrahedrally by four sulphide ions and vice versa. Such structure results when the cation: anion radius ratio is in the range 0.225 and 0.414. This 4: 4 structure is found in CuF, CuCl, CuBr, CuI, NH_4F, AgI.

It can be readily appreciated that the crystal structures will eventually get much more complicated when we move to compounds of AB_2, AB_3 etc. types.

APPENDIX II

TYPES OF CHEMICAL REACTIONS

In the chemical world we observe very many types of chemical reactions. In this appendix we include a representative classification of chemical reactions with their approximate definitions and some examples.

1. *Synthesis*: A chemical reaction among two or more elements or compounds may lead to the formation of new compounds. Such a reaction is called synthesis:

$$H_2 + Cl_2 \rightarrow 2HCl\ ;\ N_2 + 3H_2 \rightarrow 2NH_3$$

$$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

2. *Analysis*: Those chemical reactions which allow qualitative or quantitative identification of the constituents of a compound or a mixture is called analysis. For example, electrolysis of water produces two volumes of hydrogen at the cathode and one volume of oxygen at the anode. Thus we analyse water and find out that it is composed of hydrogen and oxygen in the ratio of 2 : 1 by volume:

$$2H_2O \xrightarrow{\text{electrolysis}} \underset{\text{(cathode)}}{2H_2} + \underset{\text{(anode)}}{O_2}$$

Chemical procedures have established (Chapter 29) that $NiSO_4.7H_2O$ is composed of one (gram) atom of nickel, one (gram) ion of sulphate and seven (gram) mole cules of H_2O.

3. *Decomposition*: Decomposition is a type of chemical reaction which leads to the breakdown of a chemical compound into simpler compounds or elements or both. Usually decomposition means thermal decomposition. Calcium carbonate, $CaCO_3$, decomposes on heating to quicklime, CaO, and carbon dioxide. A few examples are given below:

$$CaCO_3 \rightleftharpoons CaO + CO_2 + 42.5\ KCal$$

$$ZnSO_4.7H_2O \xrightarrow{\sim 70°C} ZnSO_4.6H_2O \xrightarrow{\sim 300°C} ZnSO_4$$

$$2ZnSO_4 \xrightarrow{\sim 850°C} 2ZnO + 2SO_2 + O_2$$

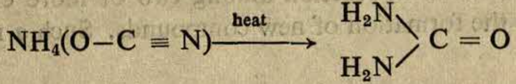
$$2KClO_3 \xrightarrow{\quad\quad} 2KCl + 3O_2$$

The chemical change brought about by electrolysis is also sometimes called electrolytic decomposition:

$$\underset{\text{(fused)}}{NaCl} \xrightarrow{\text{electrolysis}} \underset{\text{(cathode)}}{Na} + \underset{\text{(anode)}}{\tfrac{1}{2}Cl_2}$$

4. *Isomeric Change*: On the application of heat or some other chemical manipulations some compounds change into altogether new compounds with very different properties but with the same empirical composition. An isomeric change is brought about by a complete overhaul of the bonding among the different atoms and their interrelations.

An aqueous solution of ammonium cyanate on taking to dryness under heating gives urea. Both ammonium cyanate and urea have the same empirical composition but there is a hell of difference in their properties. Their structures are so very different:



$$NH_4(O-C \equiv N) \xrightarrow{\text{heat}} (H_2N)_2C=O$$

In the field of coordination compounds such isomeric changes are often observed. Thus *trans* dichloro bis (ethylenediamine) cobalt (III) chloride is green in the solid state. When this compound is dissolved in water a red-violet solution is obtained. On taking to dryness red-violet crystals of *cis* dichloro bis (ethylenediamine) cobalt (III) chloride are obtained. These two compounds are related as geometrical isomers (Chapter 6).

Isomeric change may also be termed as *molecular rearrangement*.

5. *Double Decomposition*: This is a chemical reaction between two ionic compounds that leads to an interchange of their ions and thus produces new species:

$$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2NaCl$$

$$AgNO_3 + KCl \longrightarrow AgCl + KNO_3$$

$$[Co(NH_3)_6]Cl_3 + 3KI \longrightarrow [Co(NH_3)_6]I_3 + 3KCl$$

6. *Exchange Reaction*: These are chemical interactions whereby same chemical species made of isotopes of a certain element interchange their respective positions. Thus water made of oxygen-16 and oxygen-18 are isotopic to each other. The following reaction serves as an example:

$$[Co(NH_3)_5\,(H_2O^{16})]^{3+} + H_2O^{18} \longrightarrow [Co(NH_3)_5(H_2O^{18})]^{3+}\,H_2O^{16}$$

Such an exchange reaction is, as expected, quite slow. Its half life is about 33 hours.

7. *Dissociation*: This is a type of change whereby opposite ions of an ionic compound separate under suitable conditions. Sometimes a covalent compound may also separate out into its constituent members. Such a process is different from decomposition in that it does not lead to altogether new entities but may attain equilibrium. We know water is usually a non electrolyte. But an ionic compound, on dissolution in this solvent, separates into its ions. Thus NaCl gives evidence for the the existence of sodium ion and chloride ion. Similarly H_2SO_4 gives tests for hydrogen ion and sulphate ions. Acetic acid, being a weak acid, attains equilibrium in aqueous medium

$$NaCl \xrightarrow{\text{water}} Na^+ + Cl^-$$

$$H_2SO_4 \xrightarrow{\text{water}} H^+ + HSO_4^-$$

$$CH_3COOH\ (aq) \rightleftharpoons H + CH_3COO^-$$

That such a dissociation does not lead to decomposition can be easily appreciated by noting that we can recover the sodium chloride by taking off the solvent.

On heating, gaseous HI dissociates into H_2 and I_2 and attains an equilibrium at about 180°C. On cooling HI may be recovered:

$$2HI \overset{180^\circ}{\rightleftharpoons} H_2 + I_2$$

8. *Molecular Association*: Several molecules of the same compound may be attached together through weak electrostatic forces arising out of electronegativity difference of the combining atoms. This leads to molecular association. In certain covalent compounds like HF, H_2O, NH_3 there exists considerable electronegativity difference between the interacting atoms. As a result the hydrogen end of the individual molecules become partially positive while the other end becomes partially negative. This situation leads to association of several molecules through hydrogen bonding (Chapter 5).

9. *Disproportionation*: Compounds of some metal ion in a particular oxidation state are rather unstable while compounds of the same metal in a lower and a higher oxidation state are quite stable. Under such a situation a compound of a certain oxidation state breaks up into one compound of lower oxidation state and one of higher oxidation state. Such reactions are called disproportionation:

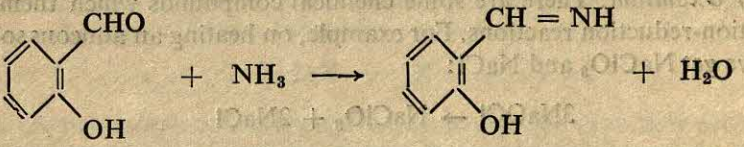
$$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + 4KOH + MnO_2$$

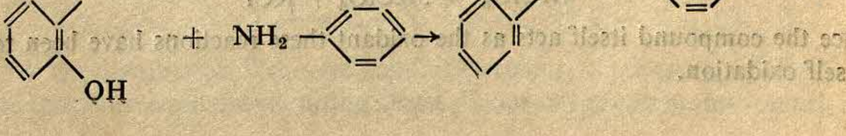
$$3Mn(VI) \rightarrow 2Mn(VII) + 1Mn(IV)\ )$$

$$2CuCl \rightarrow CuCl_2 + Cu$$

$$2U(V) \rightarrow U(VI) + U(IV)$$

10. *Condensation Reaction*: Commonly condensation reactions are those where two compounds react to form a new compound with elimination of small molecules like H_2O, NH_3 etc. These reactions are frequently made use of in the syntheses of organic compounds. Schiff bases are the condensation products of an aldehyde and an amine.





Preparation of esters from alcohols or from alcohol and acid is also loosely condensation reaction. A more apt definition is: reactions which proceed by a direct union between carbon atoms of the molecules of the same or different substances to form a new compound are called condensation reactions.

$$CH_3CH_2Br + BrCH_2CH_3 + 2Na \rightarrow CH_3CH_2CH_2CH_3 + 2NaBr$$

11. *Chain Reaction*: There are some chemical reactions where a particular participating atom, radical or a fundamental particle is regenerated. These regenerated atoms, radicals or fundamental particles can bring about a series or chain of reactions.

If a few chlorine atoms are introduced in a mixture of hydrogen and chlorine in the presence of light, then the following reactions occur:

$$Cl + H_2 \rightarrow HCl + H$$

$$H + Cl_2 \rightarrow HCl + Cl$$

The new chlorine atom so produced can initiate further reaction with hydrogen molecule producing hydrogen chloride and another chlorine atom and so on.

In the nuclear fission of uranium—235 the fundamental particle neutron initiates the chain reaction (Chapter 2). The neutron splits the uranium atom into smaller fragments alongwith fresh neutrons which bring about further fission.

$$\begin{tikzcd}
 & {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3{}^{1}_{0}n + \text{energy} \\
{}^{235}_{92}U + {}^{1}_{0}n \arrow[ur] \arrow[r] \arrow[dr] & {}^{90}_{37}Rb + {}^{144}_{55}Cs + 2{}^{1}_{0}n + \text{energy} \\
 & {}^{87}_{35}Br + {}^{146}_{57}La + 3{}^{1}_{0}n + \text{energy}
\end{tikzcd}$$

12. *Self Reduction*: When two compounds of the same metal react with each other to produce the metal in the elementary state, the reaction is called self reduction. This reaction is different from oxidation—reduction so far as the metal ion is concerned. The oxidation number of the metal in both the compounds is the same. The non-metal partners react to form a new compound leaving behind the metal. There are but very few examples of self reduction:

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

13. *Self Oxidation*: There are some chemical compounds which themselves show oxidation-reduction reactions. For example, on heating an aqueous solution of NaOCl we get $NaClO_3$ and NaCl:

$$3NaOCl \rightarrow NaClO_3 + 2NaCl$$

On heating $KClO_3$ gives $KClO_4$ and KCl:

$$4KClO_3 \rightarrow 3KClO_4 + KCl$$

Since the compound itself acts as the oxidant these reactions have been termed as self oxidation.

14. *Auto-oxidation or Induced Oxidation*: When an aqueous suspension of zinc is agitated with oxygen, zinc oxide and hydrogen peroxide are formed:

$$Zn + O_2 + H_2O \rightarrow ZnO + H_2O_2$$

It is interesting to note that no H_2O_2 is formed when oxygen is bubbled through water in the absence of zinc.

Aqueous solution of sodium arsenite is not easily oxidised in the presence of oxygen. But in the presence of a little sodium sulphite oxygen can readily oxidise sodium arsenite to arsenate.

In the above reactions oxygen react with the reducing agents to form hydrogen peroxide which then oxidises the other oxidisable substance:

$$\text{(a) } Zn + O_2 \rightarrow ZnO_2 \text{ ; } ZnO_2 + H_2O \rightarrow ZnO + H_2O_2$$

$$\text{(b) } Na_2SO_3 + O_2 + H_2O \rightarrow Na_2SO_4 + H_2O_2$$

$$Na_3AsO_3 + H_2O_2 \rightarrow Na_3AsO_4 + H_2O$$

Those reactions where otherwise stable compounds can be oxidised in the presence of a reducing agent are called auto-oxidation or induced oxidations.

In the extraction of gold the chemical reactions may be represented as (Chapter 24):

$$4Au + 2H_2O + O_2 + 8NaCN \rightarrow 4Na[Au(CN)_2] + 4NaOH$$

This reaction may also be viewed as an example of induced oxidation.

$$2Au + O_2 + H_2O \rightarrow Au_2O + H_2O_2$$

The Au_2O reacts with NaCN to give $Na[Au(CN)_2]$:

$$Au_2O + 4NaCN + H_2O \rightarrow 2Na[Au(CN)_2] + 2NaOH$$

The H_2O_2 produced in the reaction converts more of Au to Au_2O:

$$2Au + H_2O_2 \rightarrow Au_2O + H_2O$$

15. *Homolytic Cleavage and Heterolytic Cleavage*: Organic compounds are made up of covalent bonds. When organic compounds participate in chemical reactions the covalent bonds between two atoms of a given compound may break down in either of two ways: (a) a single covalent bond between two atoms has two electrons. The bond may so break down that the two electrons are distributed one each on the two atoms. Such a bond breaking through equidistribution of the two bonding electrons between the two atoms is called a homolytic cleavage:

$$X : Y \longrightarrow X\cdot + \cdot Y$$

Since the two atoms now carry one unpaired electron each they are very reactive. If the reacting system contains another free radical with one reactive unpaired electron then the following reaction may readily take place:

$$Z\cdot + X\cdot + \cdot Y \longrightarrow Z-X + (\cdot Y) \text{ or } Z-Y + (X\cdot)$$

(b) The distribution of the two bonding electrons, of necessity, will be decided by the character of the two bonding atoms. If one of the two atoms is much more electronegative then both the electrons may stay on the more electronegative partner. Such unequal distribution of the bonding electrons during a chemical reaction is known as heterolytic cleavage. In the event of a heterolytic cleavage one of the resulting species is a cation while the other is an anion:

$$X\!:\,|\,Y \longrightarrow X\!:^- + Y^+$$

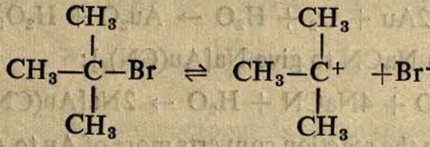
$$X\,|\,:\!Y \longrightarrow X^+ + :\!Y^-$$

It is quite likely that the anionic part will tend to attach itself to an electron loving i.e. an electrophilic reagent. On the other hand the cationic part will look out for an electron rich nucleus i.e. a nucleophilic reagent.

16. *Carbonium Ion and Carbanion*: We have earlier seen that on heterolytic cleavage a covalent bond may give rise to a cation part and an anion part. When carbon in an organic compound is attached to a strongly electronegative halogen atom, a heterolytic cleavage will produce a halide ion and a positive cationic portion containing carbon. Such a cation containing carbon is called carbonium ion. Such a cleavage leaves the electron originally on the carbon atom with the halogen. Thus ethyl bromide may undergo heterolytic cleavage to produce a carbonium ion as shown below:

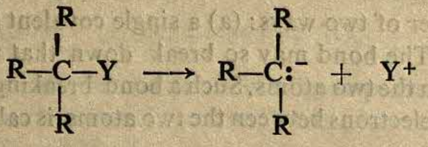
$$C_2H_5Br \rightarrow \underset{\text{(carbonium ion)}}{C_2H_5^+} + Br^-$$

A further example is also given:



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Br \rightleftharpoons CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^+}} + Br^-$$

In some other organic compounds it may so happen that the carbon atom is covalently attached to a group or atom which tends to lose electron easily. Under such a situation a heterolytic cleavage will leave an extra electron on the carbon atom making a negative anion. Such carbon containing anion is called carbanion:



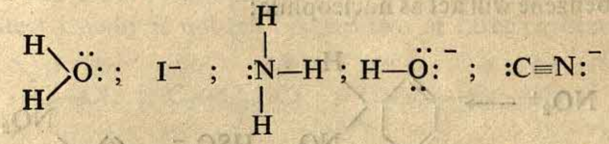
$$R-\overset{\displaystyle R}{\underset{\displaystyle R}{C}}-Y \longrightarrow R-\overset{\displaystyle R}{\underset{\displaystyle R}{C\!:^-}} + Y^+$$

It may be pointed out that the formation of both carbonium ion and carbanion is facilitated by polar solvents.

17. *Electrophilic and Nucleophilic Reactions*: There are some radicals and compounds which are electronically unsaturated. Such compounds or radicals readily take up electrons from suitable electron donors. These act as good Lewis acids. Such electron loving compounds or radicals are termed *electrophiles*. Some common examples are:

$$H^+\ (H_3O^+);\ AlCl_3;\ BF_3;\ HNO_3;\ NO_2^+;\ \text{halogens}$$

On the other side there are compounds and radicals which do possess lone pair of electrons. These species naturally seek electronically unsaturated nucleus where they can make over their lone pairs and thus bring about some chemical reactions. Such species are known as *nucleophiles*. In Chapter 6 we have seen that there are many compounds and anions with lone pairs of electrons which readily form coordination compounds with metal ions (which act as electrophiles). Some examples of nucleophiles are shown below:

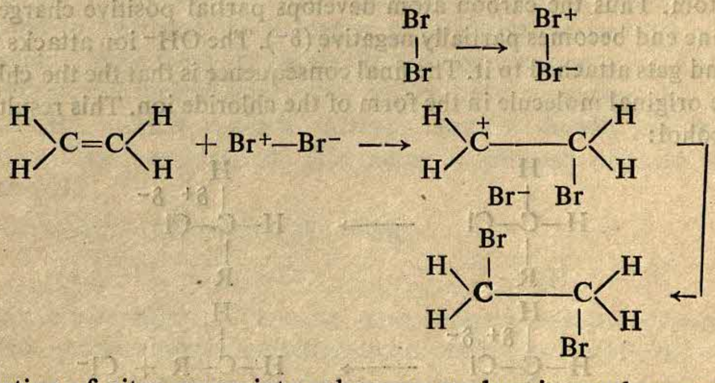


$H_2\ddot{O}:$; I^- ; $:NH_3$; $H{-}\ddot{O}:^-$; $:C{\equiv}N:^-$

It hardly needs to be mentioned that nucleophiles act as Lewis bases.

Just as oxidation and reduction reactions occur simultaneously so also the interactions between electrophiles and nucleophiles. An electrophilic reagent will take up electron from a nucleophilic reagent and vice versa. When the reagent is electrophilic in nature the corresponding reaction is called *electrophilic*. On the other hand when the reagent is nucleophilic in character the resultant reaction is termed as *nucleophilic*.

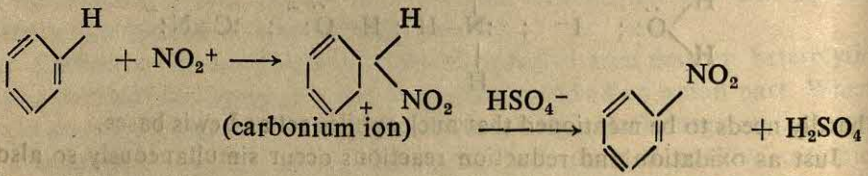
Electrophilic Reactions: In ethylene molecule there is a carbon-carbon double bond. This double bond, as we know is made up of a sigma and a pi bond. In the reactions of ethylene it is usually assumed that the two pi electrons of the double bond move over to one carbon. When ethylene is allowed to react with bromine, which is normally non-polar, the latter develops polarity when it comes close to the double bond. The double bond tends to repel the electron cloud of the bromine molecule. This repulsion makes the bromine atom nearer to the double bond positive, while the other bromine becomes negative. The Br^+ end of $Br^+{-}Br^-$ will attach itself to one of the carbon. The reaction is regarded as an electrophilic reaction because we have used bromine as a reagent. Bromine gets polarised to an electrophilic reagent and participates in the reaction as shown below. We ultimately get ethylene dibromide:



Introduction of nitro group into a benzene nucleus is another example of electrophilic reaction. We know that nitrobenzene is produced by the reaction of concentrated HNO_3 and H_2SO_4 with benzene. In this reaction NO_2^+ radical acts as the electrophile.

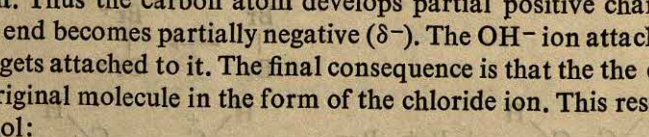
$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$$

In benzene there is resonance between the single and double bonds i.e. the electron density per bond is, on an average, more than that of a single bond. This means that in the presence of the nitronium ion, NO_2^+, acting as an electrophile, the carbon atoms in benzene will act as nucleophile:

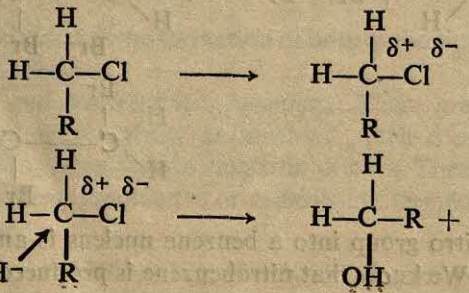


The bisulphate ion takes up a H^+ from the above carbonium ion and goes over to H_2SO_4. This is how we attempt to explain the mechanism of formation of nitrobenzene from benzene.

Nucleophilic Reactions: The reaction of a carbonyl group with hydrogen cyanide is an example of a nucleophilic reaction. The oxygen end of the carbonyl group of a ketone gets a fractional negative charge (δ^-) while the carbon end gets a similar positive charge (δ^+). The lone pair of the carbon of hydrogen cyanide gets itself attached to the positive carbon of the carbonyl group. The hydrogen ion and (δ^-) negative oxygen combine to form—OH which remains attached to the carbon. Thus cyanohydrin is formed:



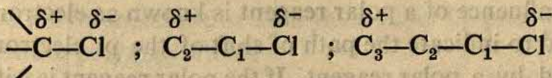
Hydroxide ion is a good nucleophile. In the presence of OH^- ion alkyl chloride is easily hydrolysed. The chlorine atom is more electronegative compared to carbon atom. Thus the carbon atom develops partial positive charge (δ^+) while the chlorine end becomes partially negative (δ^-). The OH^- ion attacks the positive carbon and gets attached to it. The final consequence is that the the chlorine atom leaves the original molecule in the form of the chloride ion. This result ultimately yields alcohol:



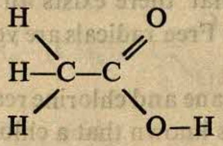
$$\begin{array}{c} H \\ | \\ H—C—Cl \\ | \\ R \end{array} \longrightarrow \begin{array}{c} H \\ |\ \delta^+\ \delta^- \\ H—C—Cl \\ | \\ R \end{array}$$

$$\begin{array}{c} H \\ |\ \delta^+\ \delta^- \\ H—C—Cl \\ \nearrow\ | \\ OH^-\ \ R \end{array} \longrightarrow \begin{array}{c} H \\ | \\ H—C—R + Cl^- \\ | \\ OH \end{array}$$

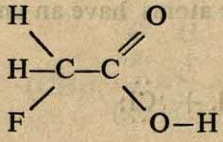
19. *Inductive Effect*: Usually if there is a covalent bond between two atoms of close electronegativity no polarity develops in the bond. However in the event of an appreciable electronegativity difference there appear a partially positive centre and a partially negative centre. Thus the electronegativities of carbon and chlorine are 2.5 and 3.0 and hence the C—Cl bond is polar in nature. If there are more carbon atoms attached to the above carbon then the influence of polarity may be transmitted to other parts of the molecule. Such transmission of partial charge from one atom to another in a molecule is called inductive effect. Such inductive effect usually is not felt beyond two or three carbon atoms.



The way properties of organic compounds are influenced by inductive effect can be seen from a comparative study of the dissociation constants of acetic acid and fluoroacetic acid:



; $K_A = 1.8 \times 10^{-5}$



; $K_A = 2.2 \times 10^{-3}$

Fluoroacetic acid is a stronger acid than acetic acid. The fluorine end of the C—F bond gets a fractional negative charge (δ^-) while a similar positive charge develops at the carbon end (δ^+). The positively charged carbon will have an inductive influence on the —COOH group. The carbon of the —COOH group will thus acquire a positive charge and hence will drag electron from the —OH group. The final outcome will be that the carboxylic acid hydrogen will dissociate more readily, making fluoroacetic acid a stronger acid than acetic acid.

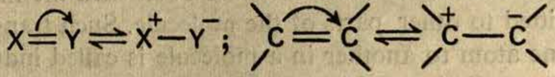
Compared to hydrogen the halogens, nitro group etc. are better electron dragging agents. Hence these groups reduce the electron density on carbon. The inductive influence of such electron attracting groups is expressed as —I. On the other hand CH_3, —CH_2R radicals increase electron density on the carbon atom to which these are attached. The inductive influence of these radicals is expressed as + I.

$+ I : -CH_3 ; -CH_2R ; -CR_3$

$-I : -F ; -Cl ; -Br ; -I ; -NO_2 ; -C_6H_5 ; -OH$

20. *Electromeric Effect*: There are many organic compounds which have multiple bonds. As we know in a multiple bond one is sigma while the others are of the pi type. Pi bonds are weaker than sigma bonds. Because of this weakness associated with pi bonds, organic compounds with multiple bonds develop polarity

when these are exposed to polar reagents. Under the influence of the polar reagent the two electrons forming a pi bond get shifted to one of the two atoms making the multiple bond. As a consequence one of the atoms becomes partially positive while the other becomes partially negative. Development of such polarity in the organic molecule makes it quite reactive. Shifting of pi electrons from one atom to another under the influence of a polar reagent is known as electromeric effect. A curved arrow is used to indicate the path of shift of the pi electrons. Electromeric effect is induced by a polar reagent. If the polar reagent is withdrawn the molecule goes back to its original state. Thus electromeric effect is but a temporary effect.



21. *Free Radical Mechanism*: A free radical is generated when a diatomic molecule or a compound so breaks down that there exists an unpaired electron on one of the atoms or the species formed. Free radicals are very reactive. These can initiate chain reaction.

Under the influence of light or heat methane and chlorine react very vigorously to form methyl chloride. In this reaction it is known that a chlorine molecule first breaks down into two chlorine atoms. These atoms have an unpaired electron on each of them. Thus they are free radicals:

$$:\ddot{\underset{\cdot\cdot}{\text{Cl}}}\text{——}\ddot{\underset{\cdot\cdot}{\text{Cl}}}: \xrightarrow[\text{(energy)}]{h\nu} :\ddot{\underset{\cdot\cdot}{\text{Cl}}}. + \cdot\ddot{\underset{\cdot\cdot}{\text{Cl}}}:$$

The very reactive chlorine radical removes one hydrogen from a methane molecule and gives rise to hydrogen chloride (HCl). A methyl free radical (CH_3) is generated in the process:

$$Cl. + CH_4 \rightarrow H{-}Cl + CH_3.$$

The methyl radical reacts with a chlorine molecule and produces methyl chloride and a chlorine atom (i.e. a chlorine free radical)

$$CH_3. + Cl{-}Cl \rightarrow CH_3Cl + Cl.$$

The liberated chlorine atom or the free radical can initiate further reaction with CH_4 producing methyl radical, which in turn reacts with another chlorine molecule to give more CH_3Cl and so on. In the above equations we have used a dot to indicate an unpaired electron on a particular atom or group i.e. to indicate a free radical.

22. *Polymerisation*: Comparatively small sized organic molecules may react under favourable conditions to produce giant sized molecules of the same empirical composition. Evidently there occurs a change in the bonding pattern during the formation of the giant molecule. Such reactions whereby a small molecule is converted into very big one with the same empirical composition is known as polymerisation. In today's life polythene is an oft-heard name and serves as an example of polymerisation. In the presence of oxygen and under pressure many

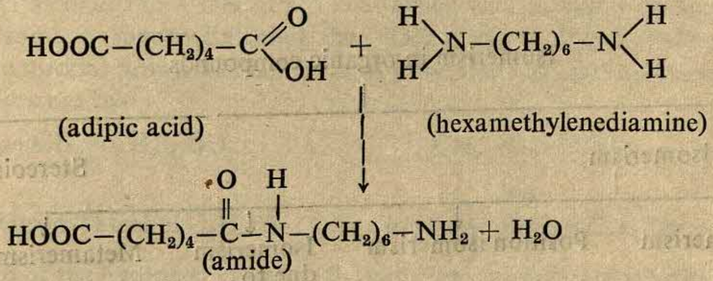
ethylene molecules interact and produce polyethylene or simply called polythene. In ethylene molecule there exists a double bond between the two carbon atoms. During polymerisation the pi bond is converted to a sigma bond which holds together carbon atoms in a chain:

$$\underset{\text{(ethylene)}}{n\,CH_2 = CH_2} \xrightarrow[\text{pressure/heat}]{\text{oxygen (catalyst)}} \underset{\text{(polyethylene)}}{-CH_2-CH_2-CH_2-CH_2-}$$

$$n\,CH_2 = CH_2 \xrightarrow{\qquad} (-CH_2-CH_2-)n$$

In the above polymerisation reaction there is no by-product. This polymerisation is called addition polymerisation.

There are examples of polymerisation reactions where H_2O, NH_3 are produced in the process of the reaction. Such polymerisation reactions are called condensation reactions. Nylon, a polymer, is produced as a result of the condensation of adipic acid and hexamethylenediamine:



$$\underset{\text{(adipic acid)}}{HOOC-(CH_2)_4-C{\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}}} + \underset{\text{(hexamethylenediamine)}}{{\begin{smallmatrix}H\searrow\\ H\nearrow\end{smallmatrix}}N-(CH_2)_6-N{\begin{smallmatrix}\nearrow H\\ \searrow H\end{smallmatrix}}}$$

$$\downarrow$$

$$\underset{\text{(amide)}}{HOOC-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_6-NH_2} + H_2O$$

The $-NH_2$ and the $-COOH$ groups of the amide react with more of the hexamethylenediamine and adipic acid to give the giant polymerised material called nylon:

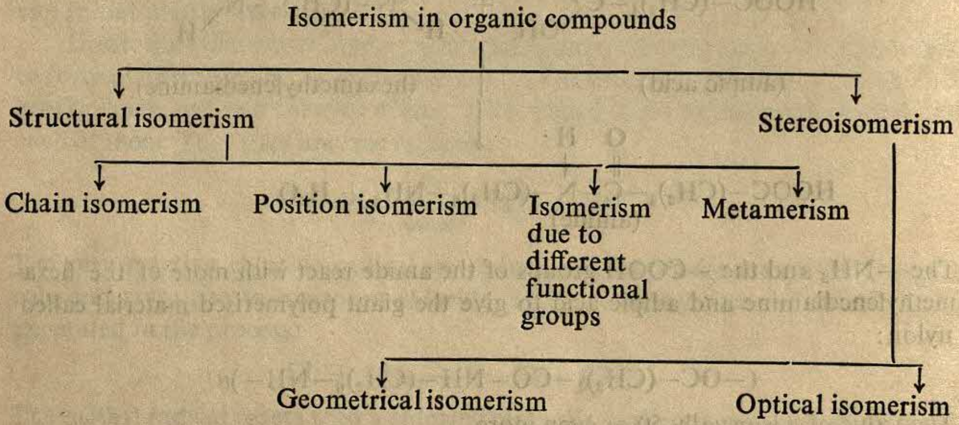
$$(-OC-(CH_2)_4-CO-NH-(CH_2)_6-NH-)n$$

The value of *n* is usually 50 or even more.

APPENDIX III

ISOMERISM IN ORGANIC COMPOUNDS

A brief account of isomerism in coordination complexes has been presented in Chapter 6. There may exist more than one compound with the same empirical composition. These compounds vary in their properties and consequently in the mutual relations among the combining atoms and evidently in the nature of bonding. This property is known as isomerism and the compounds are said to be isomeric to each other. In the domain of organic compounds we generally come across two broad types of isomerism: (a) structural isomerism and (b) stereoisomerism. These two types may be further classified. A classification is shown below:



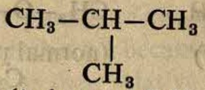
I. **Structural Isomerism:** In different organic compounds of the same empirical composition the carbon atoms and/or the other atoms or groups may be present in different orders. Such difference in arrangement gives rise to structural isomerism. A brief discussion of the different types of structural isomerism is made below:

1. *Carbon chain isomerism*: Such isomerism may arise from a difference in the mode of attachment of the various carbon atoms in the carbon-carbon chain. In normal butane (C_4H_{10}) all the carbon atoms are tetrahedral. The two intermediate carbon atoms are each linked to two hydrogen atoms and two carbon atoms. The two terminal carbon atoms are each connected to three hydrogen atoms and a carbon atom. As against this, in *iso*butane (C_4H_{10}) also all the four carbon atoms are tetrahedral. Of the four carbon atoms three are connected to three hydrogen atoms and to a central carbon atom. The central carbon atom is connected to the three other carbon atoms and a hydrogen atom. Thus in these

two hydrocarbons we do observe that there is a difference in the mode of interlinking of the carbon atoms in the carbon-carbon chain.

$CH_3-CH_2-CH_2-CH_3$

(normal butane, C_4H_{10})



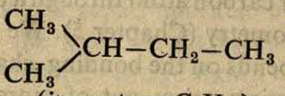
$$\begin{array}{c} CH_3-CH-CH_3 \\ | \\ CH_3 \end{array}$$

(*iso*butane, C_4H_{10})

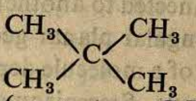
Pentane, another hydrocarbon C_5H_{12}, may exist in the following three chain isomers:

$CH_3-CH_2-CH_2-CH_2-CH_3$

(normal pentane C_5H_{12})



(*iso*pentane C_5H_{12})

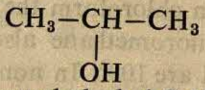


(*neo*pentane C_5H_{12})

2. *Positional Isomerism*: In these isomeric compounds the positions of the carbon atoms remain unchanged but those of the functional groups change. In normal propyl alcohol the $-OH$ group is attached to a terminal carbon atom while in the isomeric *iso*propyl alcohol the $-OH$ group is linked to the central carbon. In the normal propyl alcohol there is only one CH_3 group while in the *iso* alcohol there are two.

$CH_3-CH_2-CH_2-OH$

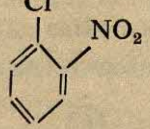
(normal propyl alcohol C_3H_8O)

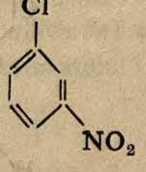


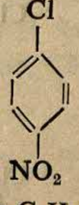
$$\begin{array}{c} CH_3-CH-CH_3 \\ | \\ OH \end{array}$$

(*iso*propyl alcohol C_3H_8O)

When two of the hydrogen atoms in the benzene molecule are substituted by a $-NO_2$ group and a $-Cl$ group we get three positional isomers. These are ortho (1 : 2), meta (1 : 3) and para (1 : 4) with respect to the relative dispositions of the $-NO_2$ and $-Cl$ groups.







(ortho $C_6H_4ClNO_2$) (meta $C_6H_4ClNO_2$) (para $C_6H_4ClNO_2$)

3. *Isomerism due to different functional groups*: There are known some organic compounds which have the same empirical composition but different functional groups. Dimethyl ether and ethyl alcohol are two simple examples of this type:

CH_3-O-CH_3 (dimethyl ether C_2H_6O)

CH_3-CH_2-OH (ethyl alcohol C_2H_6O)

4. *Metamerism*: Metamers are compounds with the same empirical composition and same functional groups but they have different alkyl groups attached to the functional groups. Some slight difference in their properties arise out of the

difference in the nature of the alkyl groups. Diethyl ether, normal propyl ether and methyl isopropyl ether form examples of metamerism.

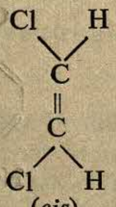
$C_2H_5-O-C_2H_5$	$CH_3-O-CH_2CH_2CH_3$	$CH_3-O-CH(CH_3)_2$
(diethyl ether)	(normal propyl ether)	(methylisopropyl ether)
$C_4H_{10}O$	$C_4H_{10}O$	$C_4H_{10}O$

II. Stereoisomerism : When a carbon atom is linked to four atoms or radical through single bonds there arises a tetrahedral geometry. But when a carbon atom is connected to another carbon atom through a double bond the molecule assumes a triangular planar geometry (Chapter 5). We thus find that the spatial arrangement of a molecule depends on the bonding character of the atoms making up the molecule. Stereoisomerism arises out of more than one three dimensional disposition of the bonding atoms or radicals in a molecule. Stereoisomerism may be of two types: (1) geometrical isomerism and (2) optical isomerism.

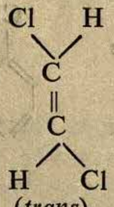
1. *Geometrical Isomerism*: It may so happen that in more than one compound with the same empirical composition and the same over-all geometry the participating atoms or radicals may have different spatial dispositions with respect to each other. Under such situation geometrical isomerism arises.

In chloroform and dichloromethane ($CHCl_3$ and CH_2Cl_2) the carbon atom is tetrahedral. In chloroform the bond angle $< H-C-Cl$ and $< Cl-C-Cl$ are 109°. In dichloromethane also the bond angles $< H-C-H$, $< H-C-Cl$ and $< Cl-C-Cl$ are 109°. In none of these two compounds geometrical isomerism can arise because all the atoms are equivalent with respect to each other.

In ethylenic compounds there is a carbon-carbon double bond and the compounds conform to triangular planar arrangement. The bond angles are 120°. In the compound 1, 2 dichloroethylene ($C_2H_2Cl_2$) the two hydrogens (as also the two chlorines) may stay as closest neighbours (*cis*) or as distant most neighbours (*trans*). These two forms are examples of geometrical isomerism:

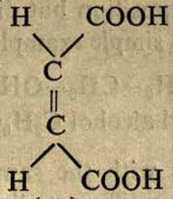


(*cis*)

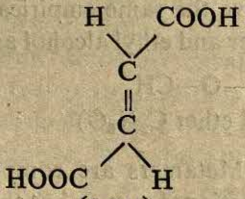


(*trans*)

Maleic acid and fumaric acid are another set of examples of geometrical isomerism in organic compounds:



(*cis*)
maleic acid



(*trans*)
fumaric acid

2. *Optical Isomerism*: We know that when a carbon atom is attached to four other atoms or radicals then the geometry about the carbon atom is tetrahedral. No geometrical isomerism can develop in compounds of the types Ca_2b_2, Ca_2bc (C carbon; a, b, c, are three different atoms or radicals.) because the a, b, c atoms or radicals are equivalent to each other so far as their relative positions are concerned ($< aCa = < aCb = < bCb$ 109°). No geometrical isomerism can be observed even when all the four attached atoms or groups are different. But compared to Ca_2b_2, Ca_2bc, the properties of the mirror image of Cabcd are different. Mirror images of Ca_2b_2 and Ca_2bc are superimposable on one another. In the following diagram if we rotate the molecule Ca_2b_2 clockwise by holding the molecule at the group *a* we get at the mirror image shown in the figure.

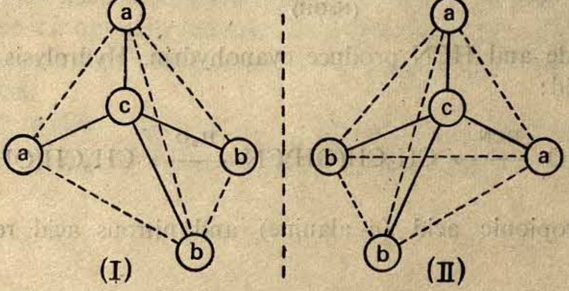


Fig. III.1. Mirror images of the tetrahedral molecule Ca_2b_2

Thus the mirror images of Ca_2b_2 do not have separate existence. But the mirror images of the molecule Cabcd are very different. One cannot be rotated to give the other. When a molecule is not superimposable on its mirror image the molecule develops optical activity. The two non-superimposable forms can rotate the plane polarised light: one to the right (dextro-rotatory) and the other to the left (laevo-rotatory). The carbon atom which has attached to itself four different groups is known as an *asymmetric* carbon atom. Lactic acid, $CH_3\overset{*}{C}H(OH)COOH$,

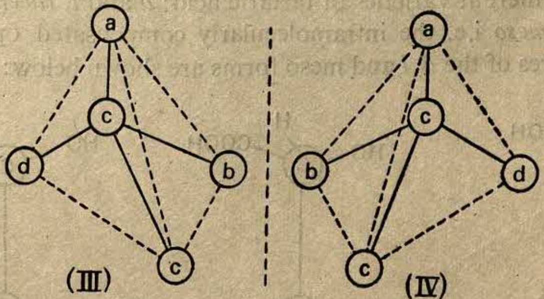


Fig. III.2. Optically active forms of tetrahedral Cabcd

has an asymmetric carbon atom marked with an asterisk. The two mirror images of lactic acid are not superimposable and hence it shows the property of optical activity. Dextrorotatory and laevorotatory lactic acids are expressed as *d* and *l* acids. When lactic acid is chemically produced it remains optically inactive because the acid then contains a mixture of 50% of dextro- and 50% of laevo acids. Thus one cancels the effect of the other. Such mixture containing equal amounts of the dextro—and laevo acids is known as *racemic mixture*. *dl* lactic acid may be obtained by the following methods. It may be mentioned that the chemicals used in the syntheses are all optically inactive and hence the lactic is also obtained in the form of inactive racemic mixture of 50% *d* and 50% *l* varieties.

α- chloropropionic acid or α- bromopropionic acid may be be hydrolysed by hot sodium hydroxide solution to get *dl* lactic acid:

$$CH_3CHBrCOOH \xrightarrow[(NaOH)]{+H_2O} CH_3CH(OH)COOH$$

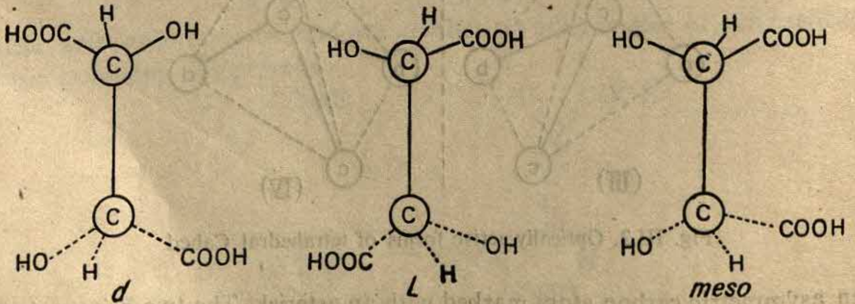
Acetaldehyde and HCN produce cyanohydrin. Hydrolysis of cyanohydrin gives *dl* lactic acid:

$$CH_3CHO \xrightarrow{HCN} CH_3CH(OH)CN \xrightarrow{H_2O} CH_3CH(OH)COOH$$

α- aminopropionic acid (α- alanine) and nitrous acid react to produce lactic acid:

$$CH_3CH(NH_2)COOH \xrightarrow{HNO_2} CH_3CH(OH)COOH + N_2 + H_2O$$

A short resume on another optically active organic acid, namely, tartaric acid will now be made. Lactic acid has only one asymmetric carbon atom while tartaric acid, $(HOOC-\overset{*}{C}H(OH)-\overset{*}{C}H(OH)COOH)$ has two asymmetric carbon atoms. As expected each of these two asymmetric carbon atoms is connected to as many as four different atoms or groups. These four are hydrogen atom, carbon atom (or rather the group $-CH(OH)COOH$), hydroxyl group and a carboxyl group. Because of the presence of the two asymmetric carbon atoms there exist as many as four different varieties of tartaric acid: *d* and *l*, *racemic* (50% *d* plus 50% *l*) and the *meso* i.e. the intramolecularly compensated optically inactive acid. The structures of the *d*, *l* and meso forms are shown below:



d *l* *meso*

Fig. III.3. The *d*, *l* and *meso* forms of tartaric acid

An inspection of the structures shows that the *d* and the *l* forms are mirror images of each other but one cannot be superimposed on the other. Thus they have separate identity and can thus generate optical activity. If the *d* tartaric acid is rotated through 120° about the carbon-carbon axis the $-COOH$ radical of the *d* acid will be shifted to the earlier position of the $-OH$ group. The $-OH$ group will be shifted to the position of H while H will go over to the position of the $-OH$ group. These changes are with respect to the upper half of the molecule. Neither the *d* nor the *l* form has any plane of symmetry or any centre of symmetry. The structure of the *meso* acid reveals that its upper half has the structure of the upper half of the *l* acid while the lower half has the orientation of the lower half of the *d* acid. Thus the upper half is the mirror image of the lower half. Thus the molecule itself compensates its optical activity arising out of the two halves and hence it is optically inactive. Thus the *meso* acid has individual existence and is different from the racemic variety which is a mixture of 50% of the *d* and 50% of the *l* acid.

Besides the optical activity of these different forms, these forms also differ in their melting points, solubility in water and in their acid dissociation constants.

APPENDIX IV

ATOMIC WEIGHTS (BASED ON $^{12}_{6}C$ 12.0000)

Element	*Symbol*	*Atomic Number*	*Atomic Weight*
Actinium	Ac	89	227
Aluminium	Al	13	26.98
Americium	Am	95	243
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.34
Berkelium	Bk	97	247
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Boron	B	5	10.81
Bromine	Br	35	79.9
Cadmium	Cd	48	112.4
Calcium	Ca	20	40.08
Californium	Cf	98	249
Carbon	C	6	12.01
Cerium	Ce	58	140.1
Caesium	Cs	55	132.9
Chlorine	Cl	17	35.45
Chromium	Cr	24	51.99
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	248.0
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	254.0
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	253.00
Fluorine	F	9	18.99
Francium	Fr	87	223
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Helium	He	2	4.00
Holmium	Ho	67	164.93

Element	*Symbol*	*Atomic Number*	*Atomic Weight*
Hydrogen	H	1	1.008
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.20
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lw	103	259
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutecium	Lu	71	174.98
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Mendeleevium	Md	101	256
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	237
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.01
Nobelium	No	102	253
Osmium	Os	76	190.2
Oxygen	O	8	15.999
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	242
Polonium	Po	84	210
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	145
Protactinium	Pa	91	231
Radium	Ra	88	226
Radon	Rn	86	222
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Samarium	Sm	62	105.53
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09

Element	*Symbol*	*Atomic Number*	*Atomic Weight*
Silver	Ag	47	107.88
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	99
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Yetterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

ADDENDA AND CORRIGENDA

Page 4, *5th line from bottom*:

$$\text{Read } \frac{X}{H} \text{ for } l/t$$

Page 12, 24*th line*:

Read 10^{-28} gm for 0^{-28} gm

Page 11. 6*th line*:

$$\text{Read } \bar{v} = \frac{1}{\lambda} \text{ for } v = \frac{1}{\lambda}$$

Page 35. *Add the following at the end of Problem* 2:

Decay constant is the fraction of atoms undergoing disintegration in unit time. Since each disintegrating atom will produce one alpha particle, we now need to calculate the total number of atoms present in 0.001 gm of radium. Number of atoms present in 1 gm is the Avogadro number divided by the mass number of the element. Hence the number of atoms present in 0.001 gm of radium is given by:

$$\frac{6.02 \times 10^{23} \times 0.001}{226}$$

Therefore the number of disintegrations per minute is:

$$\frac{6.02 \times 10^{23} \times 0.001 \times 0.8 \times 10^{-9}}{226}$$

$$\simeq 0.2 \times 10^{10}$$

Page 126. *9th line from bottom*:

Read $-\log(66.6 \times 10^{-3})$ for $-\log(66.6010^{-3})$

Page 163. 13*th line*:

Read $7H_2O$ for $7H_2$.

Page 164. *Add at the end of section* 10.3

In the light of the above discussion it will be in order to mention Mitscherlich's law on isomorphism:

The same nmber of atoms combined in the same manner produce the same crystalline form, no matter what the chemical nature of the atoms is.

Page 303. 21*st line*: Read As_2O_3 for AsO_3

Page 326. 2*nd line*: Read Na_2CO_3 for $NaCO_3$

Page 430. 17*th line*: Read 'distillation of the amalgam' for 'of the amalgam distillation'.

Page 515. 7*th line*: Read $-COOH$ for $-OH$

INDEX

Accumulator, 277
Acids and bases, 119
  Arrhenius theory, 119
  Lewis theory, 122
  Lowry—Bronsted theory, 121
Alkali elements, 217
Alkaline earth metals, 232
Alpha particle, 27
Aluminium, 251
Aluminothermite process, 255
Alums, 88
Amalgams, 423
Ammonia, 281
Anode, 108, 113
Antimony, 302
Argon, 360
Arsenic, 302
Arsenites, 304
Arsine, 302
Artificial radioactivity, 35
Artificial transmutation, 35
Atom, structure of, 1
Atomic number
  determination of, 9
Atomic orbitals, 18
  hybrid, 72
Atomic radii, 66
Atomic weight scale, 167
  determination of, 171
Auric chloride, 412
Aurous chloride, 412
Avogadro number, 5, 7
Azides, 286

Balmer spectrum, 16
Barium, 242
Bauxite, 254
Beryllium, 253
Beta decay, 33
Bessemer converter, 390
Bismuth, 306
Blast furnace, 388
Bleaching powder, 240
Bond angle, 68
Bond energy, 68
Bond length, 68
Borax, 249
  beads, 249
Borazole, 250
Boron, 246
Boric acid, 248
Brass, 408
Bromates, 352
Bromide, 351
Bromine, 353
Bronze, 271
Brown ring test, 469
Buffer solution, 138

Cadmium, 421
Calcium, 241
Calomel, 426
Carbon, 260
Carbon dating, 40
Carbon dioxide, 262
Carbon monoxide, 263
Carbonate ion, 82
Carbonyls, 263
Carborundum, 269
Caro's acid, 314
Cassiterite, 272
Catalyst, 283
Cathode, 108
Cement, Portland, 239
Chain reaction, 42
Charcoal, 159
Chlorates, 348
Chlorides, detection of, 466
Chlorine, 349
Chlorine oxides, 345
Chrome alum, 372
Chromium, 368
Chromous acetate, 372
Chromyl chloride, 370
Cinnabar, 426
Coal-gas, 261
Cobalt, 393
Common ion effect, 149
Complex salt, 87, 88
Coordinate covalence, 79
Coordination number, 87
Coordination sphere, 86–87
Copper acetate, 404
Covalent bond, 70
Cryolite, 254
Cupric ion, 403

Cuprous ion, 404
Cyanamide, 238
Cyanide process for
  silver and gold, 411, 412

Dalton, atomic theory, 1
Daniell cell, 106
Definite proportion, 168
Deuterium, 38
Diagonal relationship, 218, 253
Diamagnetism, 186
Diamond, 160
Diborane, 247
Dipole moment, 80
Disproportionation reaction, 401, 501
Dissociation constant, 127
Dulong and Petit's law, 173
Dumas, composition of water, 437

Electrical nature of matter, 1
Electrochemical series of
  elements, 111
Electron, charge, 5
  charge-to-mass ratio, 3
  mass, 6
Electron affinity, 62
Electron configuration of atoms, 21
Electroplating, 98
Electronegativity, 62
Energy levels of hydrogen atom, 16
Ethylene diamine tetraacetic
  acid, 91, 96
Extraction procedures, 191

Fajans' rules, 78
Faraday's laws of electrolysis, 5
Ferrate ion, 383
Ferric ion, 384
Ferrous ion, 385
Fission, nuclear, 42
Fluorine, 341
Freezing point depression, 179
Fuel gases, 261
Fusion, nuclear, 43

Galvanising, 421
Gamma ray, 29
Gay-Lussac, law of combining
  volumes, 168
Gay-Lussac tower, 329
Geometrical isomer, 95
Geometry of molecules, 75
German silver, 408
Giant molecules, 159
Glasses, 269
Glasses, etching of, 341
Glover tower, 328
Gold, 412
Graham's law, 38
Gram-atomic weight, 168
Gram-molecular weight, 178
Graphite, 159
Groups of periodic table,
  IA, 217
  IIA, 232
  IIIB, 245
  IVB, 258
  VB, 279
  VIB, 309
  VIIB, 339
  0, 359

Haber-Bosch process, 283
Half-life, 34
Half-reaction, 102, 108
Halogens, 339
Hardness, removal of, 212
Heavy water, 39, 203
Hydrazine, 285
Hydrazoic acid, 286
Hydrides, 207
Hydroiodic acid, 353
Hydrobromic acid, 351
Hydrochloric acid, 343
Hydrogen, 202
Hydrogen bond, 80
Hydrolith, 237
Hydroxylamine, 287
Hypochlorous acid, 347
Hyponitrites, 291
Hypophosphoric acid, 298
Hypophosphorous acid, 298

Indicators, acid-base, 137
Intermolecular attraction, 83
Iodic acid, 355
Iodine, 353
Ionic bond, 69
Ionic radius, 64
Ionisation potential, 60
Iron, 381, 383
Iron triad, 381

Isomers, 93, 94
Isotopes, 12, 38

Lanthanide elements, 23
Lattice energy, 70
Laws of electrolysis, 5
Lead, 273
Le Chatelier's principle, 140
Ligand, 87
Litharge, 273
Lithium, 218
Lithium aluminium hydride, 253
Lowry-Bronsted theory, 121

Magnesium, 234
Manganese, 374
Manganese dioxide, 378
Manganic alum, 379
Marsh test, 302
Mass spectrograph, 39
Mercuric ion, 424
Mercurous ion, 425
Mercury, 423
Metallic bond, 83
Mole, 5
Molecular orbital, 83
Molecular weight, 178
Multiple bonds, 75
Multiple proportion, 168

Nascent hydrogen, 205
Neon, 361
Nessler's reagent, 424
Nickel, 396
Nitrate ion, 292
Nitric acid, 292
Nitric oxide, 288
Nitrogen, electronic structure, 281
Nitrolim, 238
Nitrosyl-sulphuric acid, 329
Nitrous acid, 291
Noble gas compounds, 363
Nomenclature of complex
  compounds, 92
Nuclear reactions, 42
Nucleon, 12, 42
Nucleus of the atom, 7

Oil (froth) floatation process, 197
Orbitals, 2, 18, 71
Orthohydrogen, 204
Orthophosphoric acid, 299
Orthosilicate, 270
Oxidation, 102
Oxides, 311
Oxidising agents (oxidant), 102
Oxygen, 154
Ozone, 157, 320

Parahydrogen, 204
Paramagnetism, 186
Pauli exclusion principle, 17
Perchloric acid, 349
Periodic acid, 356
Periodic table, 45
Permanganate, 376
Peroxydisulphuric acid, 314
pH scale, 124
Phosphoric acid, 298
Phosphorous acid, 298
Photography, 409
Planck's constant, 13
Plaster of Paris, 238
Polythionic acids, 333
Portland cement, 239
Positron, 34
Potassium, 230
Problems, chemical, 486
Producer gas, 260
Prussian blue, 386
Pyrolusite, 380

Qualitative analysis, 446
Quantitative analysis, 473
Quartz, 266

Radioactive decay constant, 34
Radioactivity, 26
Radioelements, preparation of, 37
Radium, 429
Radon, 430
Rare-earth elements, 23
  (lanthanides)
Red lead, 273
Reduction, 99, 193
Representative elements, 21
Resonance, 82
Rutherford's scattering experiments, 7

Schonite, 88
Silica, 266
Silicates, 270
Silicic acid, 341
Silicon, 266
Silver, 408
Sodium, 220
Sodium chloride structure, 497
Solubility, 145
Specific heat, 173
Spectrograph, 39, 176
Stainless steel, 393
Standard potential, 110
Stannic acid, 272
Stannic chloride, 272
Stannous chloride, 272
Steel, 390
Strontium, 242
Structure determination, 181
Sulphur, 158
Sulphur oxides, 322
Sulphuric acid, 326
Sulphurous acid, 325
Superphosphate, 239

Thionyl chloride, 336
Thiosulphate, 332
Thorium, 431
Tin, 271
Transition elements, 21

Uncertainty principle of
  Heisenberg, 19
Ultramarine, 270
Uranium, 433

Valence, 68
Valence shell electron pair repulsion, 75
Vapour density, 171
Vitriol, 163

Water, dissociation of, 123
Water gas, 260
Wave length, 11
Wave number, 11

Xenon fluorides, 363
X-ray spectra, 10
X-ray and chemical analysis, 184

Zinc, 417
Zinc blende structure, 498

ABOUT THE BOOK

The present volume has been brought out for the benefit of the undergraduate science students of India and Bangladesh. Prof. Dutta has taken full advantage of his long teaching experience at the postgraduate and the undergraduate levels, spanning thirty years. He has always kept in view that his audience comprises B.Sc. (Pass), Chemestry (minor) and Chemistry (subsidiary) students. He has therefore not allowed the book to *grow* under his hands. The book is concise, to-the-point and yet comprehensive. The chapters break-up itself speaks of a very meticulous approach in handling the subject matter. The inclusion of two chapters on qualitative and quantitative analyses is very novel. The present volume therefore is a two-in-one book. Another speciality of the book is the huge number (over one hundred) of solved problems. Useless and time-barred descriptive materials which need only be crammed, have been dropped. Three very useful appendices appear at the end.

The author and the publisher will consider their efforts amply justified and rewarded if the student community and the teaching community find the book not only adequate for class room use but also stimulating in its style and contents. Any suggestions for further improvement of the book may kindly be forwarded to the author.

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